



Swiss Centre
for Life Cycle
Inventories

A joint initiative
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Life Cycle Inventories of Chemicals

Data v2.0 (2007)



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ecoinvent report No. 8

Dübendorf, Dezember 2007

Project "ecoinvent data v2.0"

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Life Cycle Inventories of Chemicals

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Citation:

Althaus H.-J., Chudacoff M., Hischier R., Jungbluth N., Osses M. and Primas A. (2007) Life Cycle Inventories of Chemicals. ecoinvent report No. 8, v2.0. EMPA Dübendorf, Swiss Centre for Life Cycle Inventories, Dübendorf, CH, from www.ecoinvent.org.

Comments on version 2.0

This part corresponds to the original report Althaus et al. 2004 that has been updated with the changes reported in Frischknecht et al. 2006. Direct changes in the unit process data have been made for the following datasets:

- Acetic Acid
- Acrilic Acid
- Carbon Black
- Melamine
- Polytetrafluoroethylene (PTFE)
- Silicones and Silicone Products
- Water

The chapter on Acetic Anhydride has been removed from this report since a new dataset has been established and documented in Sutter 2007b.

In the other chapters the references to the ecoinvent reports were updated and in some of the chapters the exchanges that changed names from version 1 to 2 (e.g. transports) were updated in figures and tables.

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Althaus H.-J., Chudacoff M., Hischier R., Jungbluth N., Osses M. and Primas A. (2007) Life Cycle Inventories of Chemicals. Final report ecoinvent data v2.0 No. 8. EMPA, Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.org.

Final report of the project of a National Life Cycle Inventory Database "Ecoinvent 2000" commissioned by BUWAL/BFE/ASTRA/BLW

Part I

Methodological Remarks

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Data: v2.0 (2007)

Althaus H.-J., Chudacoff M., Hischier R., Jungbluth N., Osses M. and Primas A. (2007) Life Cycle Inventories of Chemicals. Final report ecoinvent data v2.0 No. 8. EMPA, Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.org.

Final report of the project of a National Life Cycle Inventory Database "Ecoinvent 2000" commissioned by BUWAL/BFE/ASTRA/BLW

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1 Introduction

This report summarises the chemicals inventoried by the different partners in the Ecoinvent 2000 project and the updates made to these datasets for the version 2.0 of the ecoinvent Database. In each chapter of Part II one chemical or one family of chemicals is reported. Part I gives information valid for all inventories.

Chemicals that are inventoried in the context of certain materials might be included in the respective report. Thus e.g. aluminium oxide (Al_2O_3) is not included in this report but in the chapter “aluminium” in the metal report. Datasets for chemicals inventoried for version 2.0 of the ecoinvent Database are reported in Sutter 2007a; Sutter 2007b. Tab. 1.1 gives an alphabetical overview of the chemicals inventoried in ecoinvent data v2.0.

Tab. 1.1 Overview of chemicals inventoried in ecoinvent v1.0

Name	Loc	Reported in
[sulfonyl]urea-compounds, at regional storehouse	RER	Nemecek et al. 2007
[sulfonyl]urea-compounds, at regional storehouse	CH	Nemecek et al. 2007
[thio]carbamate-compounds, at regional storehouse	RER	Nemecek et al. 2007
[thio]carbamate-compounds, at regional storehouse	CH	Nemecek et al. 2007
1,1-difluoroethane, HFC-152a, at plant	US	Jungbluth & Tuchschild 2007
1,1-dimethylcyclopentane, from naphtha, at plant	RER	Jungbluth et al. 2007
1-butanol, propylene hydroformylation, at plant	RER	Sutter 2007b
1-pentanol, at plant	RER	Sutter 2007b
1-propanol, at plant	RER	Sutter 2007b
2,3-dimethylbutan, from naphtha, at plant	RER	Jungbluth et al. 2007
2,4-D, at regional storehouse	RER	Nemecek et al. 2007
2,4-D, at regional storehouse	CH	Nemecek et al. 2007
2-butanol, at plant	RER	Sutter 2007b
2-methyl-1-butanol, at plant	RER	Sutter 2007b
2-methyl-2-butanol, at plant	RER	Sutter 2007b
2-methylpentane, from naphtha, at plant	RER	Jungbluth et al. 2007
3-methyl-1-butanol, at plant	RER	Sutter 2007b
3-methyl-1-butyl acetate, at plant	RER	Sutter 2007b
4-methyl-2-pentanone, at plant	RER	Sutter 2007b
acetaldehyde, at plant	RER	Part II
acetamide-anilide-compounds, at regional storehouse	RER	Nemecek et al. 2007
acetamide-anilide-compounds, at regional storehouse	CH	Nemecek et al. 2007
acetic acid from acetaldehyde, at plant	RER	Sutter 2007b
acetic acid from butane, at plant	RER	Sutter 2007b
acetic acid, 98% in H_2O , at plant	RER	Part II
acetic anhydride from acetaldehyde, at plant	RER	Sutter 2007b
acetic anhydride from ketene, at plant	RER	Sutter 2007b
acetic anhydride, at plant	RER	Sutter 2007b
acetone cyanohydrin, at plant	RER	Part II

acetone from butane, at plant	RER	Sutter 2007b
acetone, liquid, at plant	RER	Part II
acetonitrile, at plant	RER	Sutter 2007b
acetylene, at regional storehouse	CH	Part II
acrylic acid, at plant	RER	Part II
acrylic binder, 34% in H ₂ O, at plant	RER	Part II
acrylic dispersion, 65% in H ₂ O, at plant	RER	Part II
acrylic filler, at plant	RER	Kellenberger et al. 2007
acrylic varnish, 87.5% in H ₂ O, at plant	RER	Part II
acrylonitrile from Sohio process, at plant	RER	Sutter 2007b
acrylonitrile, at plant	RER	Part II
adhesive for metals, at plant	DE	Kellenberger et al. 2007
adipic acid, at plant	RER	Part II
air separation plant	RER	Part II
air separation, cryogenic	RER	Part II
AKD sizer, in paper production, at plant	RER	Part II
alachlor, at regional storehouse	RER	Nemecek et al. 2007
alachlor, at regional storehouse	CH	Nemecek et al. 2007
alkyd paint, white, 60% in H ₂ O, at plant	RER	Part II
alkyd paint, white, 60% in solvent, at plant	RER	Part II
alkyd resin, long oil, 70% in white spirit, at plant	RER	Part II
alkylbenzene sulfonate, linear, petrochemical, at plant	RER	Zah & Hischier 2007
alkylbenzene, linear, at plant	RER	Part II
allyl chloride, from reacting propylene and chlorine, at plant	RER	Jungbluth et al. 2007
allylic chloride, at plant	RER	Part II
aluminium fluoride, at plant	RER	Part II
aluminium hydroxide, at plant	RER	Classen et al. 2007
aluminium oxide, at plant	RER	Classen et al. 2007
aluminium sulphate, powder, at plant	RER	Part II
ammonia, liquid, at regional storehouse	RER	Part II
ammonia, liquid, at regional storehouse	CH	Part II
ammonia, partial oxidation, liquid, at plant	RER	Part II
ammonia, steam reforming, liquid, at plant	RER	Part II
ammonium bicarbonate, at plant	RER	Part II
ammonium carbonate, at plant	RER	Part II
ammonium chloride from chlorosilane, at plant	GLO	Sutter 2007a
ammonium chloride, at plant	GLO	Sutter 2007a
ammonium nitrate phosphate, as N, at regional storehouse	RER	Nemecek et al. 2007
ammonium nitrate phosphate, as P ₂ O ₅ , at regional storehouse	RER	Nemecek et al. 2007
ammonium nitrate phosphate, at regional storehouse	RER	Nemecek et al. 2007
ammonium nitrate, as N, at regional storehouse	RER	Nemecek et al. 2007
ammonium sulphate, as N, at regional storehouse	RER	Nemecek et al. 2007
ammonium thiocyanate, at plant	GLO	Sutter 2007a
anhydrite rock, at mine	CH	Kellenberger et al. 2007

anhydrite, at plant	CH	Kellenberger et al. 2007
anhydrite, burned, at plant	CH	Kellenberger et al. 2007
aniline, at plant	RER	Part II
anionic resin, at plant	CH	Part II
anthraquinone, at plant	RER	Part II
argon, crude, liquid, at plant	RER	Part II
argon, liquid, at plant	RER	Part II
arsine, at plant	GLO	Sutter 2007a
atrazine, at regional storehouse	RER	Nemecek et al. 2007
atrazine, at regional storehouse	CH	Nemecek et al. 2007
barite, at plant	RER	Part II
bentonite, at processing	DE	Kellenberger et al. 2007
benzal chloride, at plant	RER	Sutter 2007b
benzaldehyde, at plant	RER	Sutter 2007b
benzene, at plant	RER	Part II
benzimidazole-compounds, at regional storehouse	RER	Nemecek et al. 2007
benzimidazole-compounds, at regional storehouse	CH	Nemecek et al. 2007
benzo[thia]diazole-compounds, at regional storehouse	RER	Nemecek et al. 2007
benzo[thia]diazole-compounds, at regional storehouse	CH	Nemecek et al. 2007
benzoic-compounds, at regional storehouse	RER	Nemecek et al. 2007
benzoic-compounds, at regional storehouse	CH	Nemecek et al. 2007
benzyl alcohol, at plant	RER	Sutter 2007b
benzyl chloride, at plant	RER	Sutter 2007b
biocides, for paper production, unspecified, at plant	RER	Part II
bipyridylum-compounds, at regional storehouse	RER	Nemecek et al. 2007
bipyridylum-compounds, at regional storehouse	CH	Nemecek et al. 2007
bisphenol A, powder, at plant	RER	Part II
Borax, anhydrous, powder, at plant	RER	Part II
boric acid, anhydrous, powder, at plant	RER	Part II
boric oxide, at plant	GLO	Sutter 2007a
boron carbide, at plant	GLO	Sutter 2007a
boron trifluoride, at plant	GLO	Sutter 2007a
butadiene, at plant	RER	Hischier 2007
butane-1,4-diol, at plant	RER	Sutter 2007b
butanes from butenes, at plant	RER	Sutter 2007b
butanol, 1-, at plant	RER	Part II
butene, mixed, at plant	RER	Hischier 2007
butyl acetate, at plant	RER	Sutter 2007b
butyl acrylate, at plant	RER	Part II
butyrolactone	GLO	Sutter 2007a
calcium ammonium nitrate, as N, at regional storehouse	RER	Nemecek et al. 2007
calcium borates, at plant	TR	Part II
calcium carbide, technical grade, at plant	RER	Part II
calcium chloride, CaCl ₂ , at plant	RER	Part II

calcium chloride, CaCl ₂ , at regional storage	CH	Part II
calcium chloride, from hypochlorination of allyl chloride, at plant	RER	Jungbluth et al. 2007
calcium nitrate, as N, at regional storehouse	RER	Nemecek et al. 2007
carbofuran, at regional storehouse	RER	Nemecek et al. 2007
carbofuran, at regional storehouse	CH	Nemecek et al. 2007
Carbon black, at plant	GLO	Part II
carbon dioxide liquid, at plant	RER	Part II
carbon disulfide, at plant	GLO	Sutter 2007a
carbon monoxide, CO, at plant	RER	Part II
carbon tetrachloride, at plant	RER	Part II
carboxymethyl cellulose, powder, at plant	RER	Zah & Hischier 2007
catalytic oxidation of benzene	RER	Part II
cationic resin, at plant	CH	Part II
cerium concentrate, 60% cerium oxide, at plant	CN	Primas 2007
chemical plant, organics	RER	Part II
chemicals inorganic, at plant	GLO	Part II
chemicals organic, at plant	GLO	Part II
chlor-alkali electrolysis, diaphragm cell	RER	Part II
chlor-alkali electrolysis, membrane cell	RER	Part II
chlor-alkali electrolysis, mercury cell	RER	Part II
chlorine dioxide, at plant	RER	Part II
chlorine, gaseous, diaphragm cell, at plant	RER	Part II
chlorine, gaseous, lithium chloride electrolysis, at plant	GLO	Sutter 2007a
chlorine, gaseous, membrane cell, at plant	RER	Part II
chlorine, gaseous, mercury cell, at plant	RER	Part II
chlorine, liquid, production mix, at plant	RER	Part II
chloroacetic acid, at plant	RER	Part II
chlorodifluoromethane, at plant	NL	Part II
chloromethyl methyl ether, at plant	RER	Part II
chromite, ore concentrate, at beneficiation	GLO	Classen et al. 2007
chromium oxide, flakes, at plant	RER	Part II
copper carbonate, at plant	RER	Part II
copper oxide, at plant	RER	Part II
crude coco nut oil, at plant	PH	Part II
crude palm kernel oil, at plant	MY	Part II
crude palm oil, at plant	MY	Part II
cryolite, at plant	RER	Part II
cumene, at plant	RER	Part II
cyanazine, at regional storehouse	RER	Nemecek et al. 2007
cyanazine, at regional storehouse	CH	Nemecek et al. 2007
cyclic N-compounds, at regional storehouse	RER	Nemecek et al. 2007
cyclic N-compounds, at regional storehouse	CH	Nemecek et al. 2007
cyclohexane, at plant	RER	Sutter 2007b
cyclohexanol, at plant	RER	Part II

cyclohexanone, at plant	RER	Sutter 2007b
DAS-1, fluorescent whitening agent triazinylaminostilben type, at plant	RER	Zah & Hischier 2007
deinking emulsion, in paper production, at plant	RER	Part II
diammonium phosphate, as N, at regional storehouse	RER	Nemecek et al. 2007
diammonium phosphate, as P2O5, at regional storehouse	RER	Nemecek et al. 2007
diammonium phosphate, at regional storehouse	RER	Nemecek et al. 2007
diborane, at plant	GLO	Sutter 2007a
dicamba, at regional storehouse	RER	Nemecek et al. 2007
dicamba, at regional storehouse	CH	Nemecek et al. 2007
dichloromethane, at plant	RER	Part II
dichloropropene, from reacting propylene and chlorine, at plant	RER	Jungbluth et al. 2007
diethanolamine, at plant	RER	Part II
diethyl ether, at plant	RER	Sutter 2007b
diethylene glycol, at plant	RER	Part II
dimethyl ether, at plant	RER	Part II
dimethyl sulfoxide, at plant	RER	Sutter 2007b
dimethyl sulphate, at plant	RER	Part II
dimethylacetamide, at plant	GLO	Sutter 2007a
dimethylamine borane, at plant	GLO	Sutter 2007a
dimethylamine, at plant	RER	Sutter 2007b
dinitroaniline-compounds, at regional storehouse	RER	Nemecek et al. 2007
dinitroaniline-compounds, at regional storehouse	CH	Nemecek et al. 2007
dioxane, at plant	RER	Sutter 2007b
diphenylether-compounds, at regional storehouse	RER	Nemecek et al. 2007
diphenylether-compounds, at regional storehouse	CH	Nemecek et al. 2007
dipropylene glycol monomethyl ether, at plant	RER	Sutter 2007a
direct oxidation of n-butane	RER	Part II
dithiocarbamate-compounds, at regional storehouse	RER	Nemecek et al. 2007
dithiocarbamate-compounds, at regional storehouse	CH	Nemecek et al. 2007
diuron, at regional storehouse	RER	Nemecek et al. 2007
diuron, at regional storehouse	CH	Nemecek et al. 2007
DTPA, diethylenetriaminepentaacetic acid, at plant	RER	Part II
EDTA, ethylenediaminetetraacetic acid, at plant	RER	Part II
epichlorhydrin, at plant	RER	Part II
epichlorhydrin, from hypochlorination of allyl chloride, at plant	RER	Jungbluth et al. 2007
esterquat, coconut oil and palm kernel oil, at plant	RER	Zah & Hischier 2007
esterquat, tallow, at plant	RER	Zah & Hischier 2007
esters of versatic acid, at plant	RER	Part II
ethanol from ethylene, at plant	RER	Sutter 2007b
ethanol, 95% in H2O, from corn, at distillery	US	Jungbluth et al. 2007
ethanol, 95% in H2O, from grass, at fermentation plant	CH	Jungbluth et al. 2007
ethanol, 95% in H2O, from potatoes, at distillery	CH	Jungbluth et al. 2007
ethanol, 95% in H2O, from rye, at distillery	RER	Jungbluth et al. 2007
ethanol, 95% in H2O, from sugar beet molasses, at distillery	CH	Jungbluth et al. 2007

ethanol, 95% in H ₂ O, from sugar beets, at fermentation plant	CH	Jungbluth et al. 2007
ethanol, 95% in H ₂ O, from sugar cane, at fermentation plant	BR	Jungbluth et al. 2007
ethanol, 95% in H ₂ O, from sugarcane molasses, at sugar refinery	BR	Jungbluth et al. 2007
ethanol, 95% in H ₂ O, from sweet sorghum, at distillery	CN	Jungbluth et al. 2007
ethanol, 95% in H ₂ O, from whey, at fermentation plant	CH	Jungbluth et al. 2007
ethanol, 95% in H ₂ O, from wood, at distillery	CH	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, at distillation	CH	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, at distillation	BR	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, at distillation	US	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, at distillation	RER	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, at distillation	CN	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, at service station	CH	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, production BR, at service station	CH	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, production CN, at service station	CH	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, production RER, at service station	CH	Jungbluth et al. 2007
ethanol, 99.7% in H ₂ O, from biomass, production US, at service station	CH	Jungbluth et al. 2007
ethanolamines, production	RER	Part II
ethoxylated alcohols (AE11), palm oil, at plant	RER	Zah & Hischier 2007
ethoxylated alcohols (AE3), coconut oil, at plant	RER	Zah & Hischier 2007
ethoxylated alcohols (AE3), palm kernel oil, at plant	RER	Zah & Hischier 2007
ethoxylated alcohols (AE3), petrochemical, at plant	RER	Zah & Hischier 2007
ethoxylated alcohols (AE7), coconut oil, at plant	RER	Zah & Hischier 2007
ethoxylated alcohols (AE7), palm kernel oil, at plant	RER	Zah & Hischier 2007
ethoxylated alcohols (AE7), petrochemical, at plant	RER	Zah & Hischier 2007
ethoxylated alcohols, unspecified, at plant	RER	Zah & Hischier 2007
ethyl acetate from butane, at plant	RER	Sutter 2007b
ethyl acetate, at plant	RER	Sutter 2007b
ethyl benzene, at plant	RER	Part II
ethyl tert-butyl ether, from bioethanol, at plant	RER	Jungbluth et al. 2007
ethylene dichloride, at plant	RER	Part II
ethylene glycol diethyl ether, at plant	RER	Sutter 2007b
ethylene glycol dimethyl ether, at plant	RER	Sutter 2007b
ethylene glycol monoethyl ether, at plant	RER	Sutter 2007b
ethylene glycol, at plant	RER	Part II
ethylene oxide, at plant	RER	Part II
ethylene oxide, at plant	RER	Sutter 2007b
ethylene, average, at plant	RER	Hischier 2007
ethylene, pipeline system, at plant	RER	Hischier 2007
ethylenediamine, at plant	RER	Part II
explosives, tovex, at plant	CH	Kellenberger et al. 2007
fatty acids, from vegetarian oil, at plant	RER	Part II
fatty alcohol sulfonate, coconut oil, at plant	RER	Zah & Hischier 2007

fatty alcohol sulfonate, mix, at plant	RER	Zah & Hischier 2007
fatty alcohol sulfonate, palm oil, at plant	RER	Zah & Hischier 2007
fatty alcohol sulfonate, palm kernel oil, at plant	RER	Zah & Hischier 2007
fatty alcohol sulfonate, petrochemical, at plant	RER	Zah & Hischier 2007
fatty alcohol, from coconut oil, at plant	RER	Part II
fatty alcohol, from palm kernel oil, at plant	RER	Part II
fatty alcohol, from palm oil, at plant	RER	Part II
fatty alcohol, petrochemical, at plant	RER	Part II
fluorescent whitening agent distyrylbiphenyl type, at plant	RER	Zah & Hischier 2007
fluorine, liquid, at plant	RER	Part II
fluorspar, 97%, at plant	GLO	Part II
fluosilicic acid, 22% in H ₂ O, at plant	RER	Part II
fluosilicic acid, 22% in H ₂ O, at plant	MA	Part II
fluosilicic acid, 22% in H ₂ O, at plant	US	Part II
flux, wave soldering, at plant	GLO	Hischier et al. 2007
formaldehyde, production mix, at plant	RER	Part II
formic acid from butane, at plant	RER	Sutter 2007b
formic acid from methyl formate, at plant	RER	Sutter 2007b
formic acid, at plant	RER	Sutter 2007b
fraction 1, from naphtha, at plant	RER	Jungbluth et al. 2007
fraction 7, from naphtha, at plant	RER	Jungbluth et al. 2007
fraction 8, from naphtha, at plant	RER	Jungbluth et al. 2007
glycerine, from epichlorohydrin, at plant	RER	Jungbluth et al. 2007
glycerine, from palm oil, at esterification plant	MY	Jungbluth et al. 2007
glycerine, from rape oil, at esterification plant	CH	Jungbluth et al. 2007
glycerine, from rape oil, at esterification plant	RER	Jungbluth et al. 2007
glycerine, from soybean oil, at esterification plant	US	Jungbluth et al. 2007
glycerine, from soybean oil, at esterification plant	BR	Jungbluth et al. 2007
glycerine, from vegetable oil, at esterification plant	FR	Jungbluth et al. 2007
glyphosate, at regional storehouse	RER	Nemecek et al. 2007
glyphosate, at regional storehouse	CH	Nemecek et al. 2007
graphite, at plant	RER	Part II
helium, at plant	GLO	Sutter 2007a
helium, gaseous, at plant	RER	Part II
heptane, at plant	RER	Jungbluth et al. 2007
hexafluorethane, at plant	GLO	Sutter 2007a
hexamethyldisilazane, at plant	GLO	Sutter 2007a
hexane, at plant	RER	Jungbluth et al. 2007
hydrochloric acid from benzene chlorination, at plant	RER	Sutter 2007b
hydrochloric acid, 30% in H ₂ O, at plant	RER	Part II
hydrochloric acid, 36% in H ₂ O, from reacting propylene and chlorine, at plant	RER	Jungbluth et al. 2007
hydrochloric acid, from Mannheim process, at plant	RER	Part II
hydrochloric acid, from the reaction of hydrogen with chlorine, at plant	RER	Part II

hydrogen cyanide from Sohio process, at plant	RER	Sutter 2007b
hydrogen cyanide, at plant	RER	Part II
hydrogen fluoride, at plant	GLO	Part II
hydrogen peroxide, 50% in H ₂ O, at plant	RER	Part II
hydrogen sulphide, H ₂ S, at plant	RER	Hischier et al. 2007
hydrogen, cracking, APME, at plant	RER	Part II
hydrogen, from butanediol dehydrogenation	GLO	Sutter 2007a
hydrogen, liquid, at plant	RER	Part II
hydrogen, liquid, diaphragm cell, at plant	RER	Part II
hydrogen, liquid, from chlorine electrolysis, production mix, at plant	RER	Part II
hydrogen, liquid, membrane cell, at plant	RER	Part II
hydrogen, liquid, mercury cell, at plant	RER	Part II
ilmenite, 54% titanium dioxide, at plant	AU	Primas 2007
intral, at plant	RER	Part II
iron (III) chloride, 40% in H ₂ O, at plant	CH	Part II
Iron-nickel-chromium alloy, at plant	RER	Part II
iron sulphate, at plant	RER	Part II
isobutanol, at plant	RER	Sutter 2007b
isobutyl acetate, at plant	RER	Sutter 2007b
isohexane, at plant	RER	Sutter 2007b
isopropanol, at plant	RER	Part II
isopropyl acetate, at plant	RER	Sutter 2007b
kaolin, at plant	RER	Part II
krypton, gaseous, at plant	RER	Part II
krypton, gaseous, at regional storage	CH	Part II
lanthanum oxide, at plant	CN	Primas 2007
latex, at plant	RER	Part II
layered sodium silicate, SKS-6, powder, at plant	RER	Zah & Hischier 2007
lime from lithium carbonate hydration	GLO	Sutter 2007a
lime, algae, at regional storehouse	CH	Nemecek et al. 2007
lime, from carbonation, at regional storehouse	CH	Nemecek et al. 2007
lime, hydrated, loose, at plant	CH	Kellenberger et al. 2007
lime, hydrated, packed, at plant	CH	Kellenberger et al. 2007
linuron, at regional storehouse	RER	Nemecek et al. 2007
linuron, at regional storehouse	CH	Nemecek et al. 2007
liquid storage tank, chemicals, organics	CH	Part II
lithium carbonate, at plant	GLO	Sutter 2007a
lithium chloride, at plant	GLO	Sutter 2007a
lithium hydroxide, at plant	GLO	Sutter 2007a
lithium manganese oxide, at plant	GLO	Sutter 2007a
lubricating oil, at plant	RER	Part II
magnesium oxide, at plant	RER	Part II
magnesium sulphate, at plant	RER	Part II
maleic anhydride from catalytic oxidation of benzene, at plant	RER	Part II

maleic anhydride from the direct oxidation of n-butane, at plant	RER	Part II
maleic anhydride, at plant	RER	Part II
malusil, at plant	RER	Part II
maneb, at regional storehouse	RER	Nemecek et al. 2007
maneb, at regional storehouse	CH	Nemecek et al. 2007
MCPA, at regional storehouse	RER	Nemecek et al. 2007
MCPA, at regional storehouse	CH	Nemecek et al. 2007
melamine formaldehyde resin, at plant	RER	Part II
melamine, at plant	RER	Part II
methane, 96 vol-%, from biogas, at purification	CH	Jungbluth et al. 2007
methane, 96 vol-%, from biogas, from high pressure network, at service station	CH	Jungbluth et al. 2007
methane, 96 vol-%, from biogas, from low pressure network, at service station	CH	Jungbluth et al. 2007
methane, 96 vol-%, from biogas, from medium pressure network, at service station	CH	Jungbluth et al. 2007
methane, 96 vol-%, from biogas, high pressure, at consumer	CH	Jungbluth et al. 2007
methane, 96 vol-%, from biogas, low pressure, at consumer	CH	Jungbluth et al. 2007
methane, 96 vol-%, from biogas, production mix, at service station	CH	Jungbluth et al. 2007
methane, 96 vol.-%, from synthetic gas, wood, at plant	CH	Jungbluth et al. 2007
methanol plant	GLO	Part II
methanol, at plant	GLO	Part II
methanol, at regional storage	CH	Part II
methanol, from biomass, at regional storage	CH	Jungbluth et al. 2007
methanol, from synthetic gas, at plant	CH	Jungbluth et al. 2007
methyl acetate from butane, at plant	RER	Sutter 2007b
methyl acetate, at plant	RER	Sutter 2007b
methyl acrylate, at plant	GLO	Sutter 2007a
methyl ethyl ketone from butane, at plant	RER	Sutter 2007b
methyl ethyl ketone, at plant	RER	Part II
methyl formate, at plant	RER	Sutter 2007b
methyl methacrylate, at plant	RER	Hischier 2007
methyl tert-butyl ether, at plant	RER	Part II
methyl-3-methoxypropionate, at plant	GLO	Sutter 2007a
methylchloride, at plant	WEU	Part II
methylchloride, at regional storage	CH	Part II
methylcyclohexane, at plant	RER	Sutter 2007b
methylcyclohexane, from naphtha, at plant	RER	Jungbluth et al. 2007
methylcyclopentane, from naphtha, at plant	RER	Jungbluth et al. 2007
methylene diphenyl diisocyanate, at plant	RER	Hischier 2007
metolachlor, at regional storehouse	RER	Nemecek et al. 2007
metolachlor, at regional storehouse	CH	Nemecek et al. 2007
monoammonium phosphate, as N, at regional storehouse	RER	Nemecek et al. 2007
monoammonium phosphate, as P2O5, at regional storehouse	RER	Nemecek et al. 2007
monoammonium phosphate, at regional storehouse	RER	Nemecek et al. 2007
monochlorobenzene, at plant	RER	Sutter 2007b

monochloropentafluoroethane, at plant	GLO	Sutter 2007a
monoethanolamine, at plant	RER	Part II
N,N-dimethylformamide, at plant	RER	Sutter 2007b
naphtha, APME mix, at refinery	RER	Hischier 2007
natural gas liquids, from natural gas, helium extraction	GLO	Sutter 2007a
neodymium oxide, at plant	CN	Primas 2007
nitric acid, 50% in H ₂ O, at plant	RER	Part II
nitrile-compounds, at regional storehouse	RER	Nemecek et al. 2007
nitrile-compounds, at regional storehouse	CH	Nemecek et al. 2007
nitrobenzene, at plant	RER	Part II
nitro-compounds, at regional storehouse	RER	Nemecek et al. 2007
nitro-compounds, at regional storehouse	CH	Nemecek et al. 2007
nitrogen, liquid, at plant	RER	Part II
N-methyl-2-pyrrolidone, at plant	RER	Sutter 2007b
n-olefins, at plant	RER	Part II
o-dichlorobenzene, at plant	RER	Sutter 2007b
optical brighteners, in paper production, at plant	RER	Part II
organophosphorus-compounds, at regional storehouse	RER	Nemecek et al. 2007
organophosphorus-compounds, at regional storehouse	CH	Nemecek et al. 2007
oxidation of methanol	RER	Part II
oxygen, liquid, at plant	RER	Part II
ozone, liquid, at plant	RER	Part II
palm kernel oil, at oil mill	MY	Jungbluth et al. 2007
palm methyl ester, at esterification plant	MY	Jungbluth et al. 2007
palm methyl ester, production MY, at service station	CH	Jungbluth et al. 2007
palm oil, at oil mill	MY	Jungbluth et al. 2007
paraffin, at plant	RER	Part II
parathion, at regional storehouse	RER	Nemecek et al. 2007
parathion, at regional storehouse	CH	Nemecek et al. 2007
p-dichlorobenzene, at plant	RER	Sutter 2007b
penta-erythritol, at plant	RER	Part II
pentane, at plant	RER	Part II
pesticide unspecified, at regional storehouse	RER	Nemecek et al. 2007
pesticide unspecified, at regional storehouse	CH	Nemecek et al. 2007
petrol, 15% vol. ETBE additive, EtOH f. biomass, prod. RER, at service station	CH	Jungbluth et al. 2007
petrol, 15% vol. ETBE additive, with ethanol from biomass, at refinery	RER	Jungbluth et al. 2007
petrol, 4% vol. ETBE additive, EtOH f. biomass, prod. RER, at service station	CH	Jungbluth et al. 2007
petrol, 4% vol. ETBE additive, with ethanol from biomass, at refinery	RER	Jungbluth et al. 2007
petrol, 5% vol. ethanol, from biomass, at service station	CH	Jungbluth et al. 2007
petrol, 85% vol. ethanol, from biomass, at service station	CH	Jungbluth et al. 2007
phenol, at plant	RER	Part II
phenolic resin, at plant	RER	Part II
phenoxy-compounds, at regional storehouse	RER	Nemecek et al. 2007

phenoxy-compounds, at regional storehouse	CH	Nemecek et al. 2007
phosgene, liquid, at plant	RER	Part II
phosphane, at plant	GLO	Sutter 2007a
phosphate rock mine	US	Part II
phosphate rock mine	MA	Part II
phosphate rock, as P2O5, beneficiated, dry, at plant	MA	Part II
phosphate rock, as P2O5, beneficiated, wet, at plant	US	Part II
phosphoric acid plant, fertiliser grade	US	Part II
phosphoric acid production, dihydrate process	MA	Part II
phosphoric acid production, dihydrate process	US	Part II
phosphoric acid, fertiliser grade, 70% in H2O, at plant	GLO	Part II
phosphoric acid, fertiliser grade, 70% in H2O, at plant	US	Part II
phosphoric acid, fertiliser grade, 70% in H2O, at plant	MA	Part II
phosphoric acid, industrial grade, 85% in H2O, at plant	RER	Part II
phosphorous chloride, at plant	RER	Part II
phosphorus, white, liquid, at plant	RER	Part II
phosphoryl chloride, at plant	RER	Sutter 2007a
ptalamide-compounds, at regional storehouse	RER	Nemecek et al. 2007
ptalamide-compounds, at regional storehouse	CH	Nemecek et al. 2007
phthalic anhydride, at plant	RER	Part II
pigments, paper production, unspecified, at plant	RER	Part II
pitch desperferts, in paper production, at plant	RER	Part II
polycarboxylates, 40% active substance, at plant	RER	Zah & Hischier 2007
polyester resin, unsaturated, at plant	RER	Part II
polyols, at plant	RER	Hischier 2007
polyphenylene sulfide, at plant	GLO	Hischier 2007
portachrom, at plant	RER	Part II
portafer, at plant	RER	Part II
potassium carbonate, at plant	GLO	Sutter 2007a
potassium chloride, as K2O, at regional storehouse	RER	Nemecek et al. 2007
potassium hydroxide, at regional storage	RER	Jungbluth et al. 2007
potassium nitrate, as K2O, at regional storehouse	RER	Nemecek et al. 2007
potassium nitrate, as N, at regional storehouse	RER	Nemecek et al. 2007
potassium nitrate, at regional storehouse	RER	Nemecek et al. 2007
potassium perchlorate, at plant	GLO	Sutter 2007a
potassium sulphate, as K2O, at regional storehouse	RER	Nemecek et al. 2007
potassium sulphate, as K2O, from rape oil, at esterification plant	RER	Jungbluth et al. 2007
praseodymium oxide, at plant	CN	Primas 2007
printing colour, offset, 47.5% solvent, at plant	RER	Part II
printing colour, rotogravure, 55% toluene, at plant	RER	Part II
propachlor, at regional storehouse	RER	Nemecek et al. 2007
propachlor, at regional storehouse	CH	Nemecek et al. 2007
propanal, at plant	RER	Sutter 2007b
propylene glycol, liquid, at plant	RER	Part II

propylene oxide, liquid, at plant	RER	Part II
propylene, at plant	RER	Hischier 2007
pyretroid-compounds, at regional storehouse	RER	Nemecek et al. 2007
pyretroid-compounds, at regional storehouse	CH	Nemecek et al. 2007
pyridazine-compounds, at regional storehouse	RER	Nemecek et al. 2007
pyridazine-compounds, at regional storehouse	CH	Nemecek et al. 2007
rape methyl ester, at esterification plant	CH	Jungbluth et al. 2007
rape methyl ester, at esterification plant	RER	Jungbluth et al. 2007
rape methyl ester, at regional storage	CH	Jungbluth et al. 2007
rape methyl ester, production RER, at service station	CH	Jungbluth et al. 2007
rape oil, at oil mill	CH	Jungbluth et al. 2007
rape oil, at oil mill	RER	Jungbluth et al. 2007
rare earth concentrate, 70% REO, from bastnasite, at beneficiation	CN	Part II
reaction of formaldehyde with acetaldehyde	RER	Part II
refrigerant R134a, at plant	RER	Heck 2007
retention aids, in paper production, at plant	RER	Part II
rosin size, in paper production, at plant	RER	Part II
rutile, 95% titanium dioxide, at plant	AU	Primas 2007
sales gas, from natural gas, helium extraction	GLO	Sutter 2007a
samarium europium gadolinium concentrate, 94% rare earth oxide, at plant	CN	Primas 2007
secondary sulphur, at refinery	RER	Part II
secondary sulphur, at refinery	CH	Part II
selenium, at plant	RER	Part II
silicon carbide, at plant	RER	Part II
silicon carbide, recycling, at plant	RER	Jungbluth & Tuchschild 2007
silicon tetrachloride, at plant	DE	Part II
silicon tetrahydride, at plant	RER	Sutter 2007a
silicone plant	RER	Part II
silicone product, at plant	RER	Part II
single superphosphate, as P2O5, at regional storehouse	RER	Nemecek et al. 2007
soap, at plant	RER	Zah & Hischier 2007
soda, powder, at plant	RER	Part II
sodium arsenide, at plant	GLO	Sutter 2007a
sodium borates, at plant	US	Part II
sodium carbonate from ammonium chloride production, at plant	GLO	Sutter 2007a
sodium chlorate, powder, at plant	RER	Part II
sodium chloride, brine solution, at plant	RER	Part II
sodium chloride, powder, at plant	RER	Part II
sodium cyanide, at plant	RER	Part II
sodium dichromate, at plant	RER	Part II
sodium dithionite, anhydrous, at plant	RER	Part II
sodium formate, reaction of formaldehyde with acetaldehyde, at plant	RER	Part II
sodium hydroxide, 50% in H2O, diaphragm cell, at plant	RER	Part II

sodium hydroxide, 50% in H ₂ O, membrane cell, at plant	RER	Part II
sodium hydroxide, 50% in H ₂ O, mercury cell, at plant	RER	Part II
sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	Part II
sodium hypochlorite, 15% in H ₂ O, at plant	RER	Part II
sodium metasilicate pentahydrate, 58%, powder, at plant	RER	Zah & Hischier 2007
sodium methoxide, at plant	GLO	Sutter 2007a
sodium perborate, monohydrate, powder, at plant	RER	Zah & Hischier 2007
sodium perborate, tetrahydrate, powder, at plant	RER	Zah & Hischier 2007
sodium percarbonate, powder, at plant	RER	Zah & Hischier 2007
sodium perchlorate, at plant	GLO	Sutter 2007a
sodium persulfate, at plant	GLO	Sutter 2007a
sodium phosphate, at plant	RER	Part II
sodium silicate, furnace liquor, 37% in H ₂ O, at plant	RER	Part II
sodium silicate, furnace process, pieces, at plant	RER	Part II
sodium silicate, hydrothermal liquor, 48% in H ₂ O, at plant	RER	Part II
sodium silicate, spray powder 80%, at plant	RER	Part II
sodium sulphat from viscose production, at plant	GLO	Althaus et al. 2007
sodium sulphate from sulfuric acid digestion of spodumene	GLO	Sutter 2007a
sodium sulphate production, Mannheim process, at plant	RER	Part II
sodium sulphate, from Mannheim process, at plant	RER	Part II
sodium sulphate, from natural sources, at plant	RER	Part II
sodium sulphate, powder, production mix, at plant	RER	Part II
sodium tetrafluorborate, at plant	GLO	Sutter 2007a
sodium tetrahydroborate, at plant	GLO	Sutter 2007a
sodium tripolyphosphate, at plant	RER	Zah & Hischier 2007
solvents, organic, unspecified, at plant	GLO	Part II
soya oil, at plant	RER	Part II
soya oil, production	RER	Part II
soya scrap, at plant	RER	Part II
soybean methyl ester, at esterification plant	US	Jungbluth et al. 2007
soybean methyl ester, at esterification plant	BR	Jungbluth et al. 2007
soybean methyl ester, production BR, at service station	CH	Jungbluth et al. 2007
soybean methyl ester, production US, at service station	CH	Jungbluth et al. 2007
soybean oil, at oil mill	US	Jungbluth et al. 2007
soybean oil, at oil mill	BR	Jungbluth et al. 2007
spodumene, at plant	RER	Part II
steam from catalytic oxidation of benzene, at plant	RER	Part II
steam from direct oxidation of n-butane, at plant	RER	Part II
steam from the production of formaldehyde	RER	Part II
steam, for chemical processes, at plant	RER	Zah & Hischier 2007
stone meal, at regional storehouse	CH	Nemecek et al. 2007
storage building, chemicals, solid	CH	Part II
styrene, at plant	RER	Hischier 2007
sulphite, at plant	RER	Part II

sulphur dioxide, liquid, at plant	RER	Part II
sulphur hexafluoride, liquid, at plant	RER	Part II
sulphur trioxide, at plant	RER	Part II
sulphuric acid from viscose production, at plant	GLO	Althaus et al. 2007
sulphuric acid, liquid, at plant	RER	Part II
tetrachloroethylene, at plant	WEU	Part II
tetrachloroethylene, at regional storage	CH	Part II
tetrachlorosilane, at plant	GLO	Sutter 2007a
tetrafluoroethylene film, on glass	RER	Part II
tetrafluoroethylene, at plant	RER	Part II
tetrahydrofuran, at plant	RER	Sutter 2007b
thomas meal, as P2O5, at regional storehouse	RER	Nemecek et al. 2007
titanium dioxide at plant, sulphate process, at plant	RER	Part II
titanium dioxide, chloride process, at plant	RER	Part II
titanium dioxide, production mix, at plant	RER	Part II
toluene diisocyanate, at plant	RER	Hischier 2007
toluene, liquid, at plant	RER	Part II
triazine-compounds, at regional storehouse	RER	Nemecek et al. 2007
triazine-compounds, at regional storehouse	CH	Nemecek et al. 2007
trichloroborane, at plant	GLO	Sutter 2007a
trichloroethylene, at plant	WEU	Part II
trichloromethane, at plant	RER	Part II
trichloropropane, from hypochlorination of allyl chloride, at plant	RER	Jungbluth et al. 2007
triethanolamine, at plant	RER	Part II
triethylene glycol, at plant	RER	Part II
triethylene glycol, recycling, at plant	RER	Jungbluth & Tuchschmid 2007
trifluoromethane, at plant	GLO	Sutter 2007a
trimethyl borate, at plant	GLO	Sutter 2007a
trimethylamine, at plant	RER	Part II
triple superphosphate, as P2O5, at regional storehouse	RER	Nemecek et al. 2007
urea ammonium nitrate, as N, at regional storehouse	RER	Nemecek et al. 2007
urea formaldehyde resin, at plant	RER	Part II
urea, as N, at regional storehouse	RER	Nemecek et al. 2007
vegetable oil methyl ester, at esterification plant	FR	Jungbluth et al. 2007
vegetable oil methyl ester, production FR, at service station	CH	Jungbluth et al. 2007
vegetable oil, from waste cooking oil, at plant	CH	Jungbluth et al. 2007
vegetable oil, from waste cooking oil, at plant	FR	Jungbluth et al. 2007
vinyl acetate, at plant	RER	Hischier 2007
vinyl chloride, at plant	RER	Hischier 2007
vinylfluoride, at plant	US	Jungbluth & Tuchschmid 2007
water, completely softened, at plant	RER	Part II
water, decarbonised, at plant	RER	Part II
water, deionised, at plant	CH	Part II

white spirit, at plant	RER	Part II
wood preservative, creosote, at plant	RER	Werner et al. 2007
wood preservative, inorganic salt, containing Cr, at plant	RER	Werner et al. 2007
wood preservative, organic salt, Cr-free, at plant	RER	Werner et al. 2007
xenon krypton purification process	RER	Part II
xenon, gaseous, at plant	RER	Part II
xenon, gaseous, at regional storage	CH	Part II
xylene, at plant	RER	Part II
zeolite, powder, at plant	RER	Zah & Hischier 2007
zeolite, slurry, 50% in H ₂ O, at plant	RER	Zah & Hischier 2007
zinc monosulphate, ZnSO ₄ .H ₂ O, at plant	RER	Hischier et al. 2007
zinc oxide, at plant	RER	Hischier et al. 2007
zinc sulphide, ZnS, at plant	RER	Hischier et al. 2007
zircon, 50% zirconium, at plant	AU	Part II
zirconium oxide, at plant	AU	Part II

2 Infrastructure for production of chemicals

Environmental burdens of the infrastructure directly needed for the production of chemicals (buildings, machines, facilities...) are of minor importance compared to the burdens of the processes themselves. Thus the infrastructure can be inventoried rather roughly. To do so, the following modules are generated:

Tab. 2.1 Modules for use in infrastructure processes for the production of chemicals

Name	Location	Unit	Comment
Building, multi story	RER	m ³	Average massive multi story buildings e.g. for offices, laboratories etc. For more details see Kellenberger et al. 2007.
Building, hall	RER	m ²	Average wood / steel frame hall e.g. for factories, warehouses etc. For more details see Kellenberger et al. 2007.
Facilities, chemical production	RER	kg	Average production facilities for chemicals per kg of the facilities. This module includes the materials and processes for manufacturing and installing the facilities including their foundations. The dismantling and disposal of the facilities is not included.
Electronics for control units	RER	kg	Average composition of a control unit - consisting of housing, cables, mounted printed wiring board (PWB) with capacitors, resistances, relays, transistors, IC's, etc. Production efforts for the various parts are included in the respective datasets this dataset is linked to – no efforts for the final assembly is taken into account in this dataset here.
Disposal, electronics for control units	RER	kg	This module includes the dismantling of the control equipment (PWB together with housing, cables, etc.).
Disposal, facilities, chemical production	RER	kg	This module includes the processes used for dismantling and disposal of the production facilities for chemicals per kg of the facilities.

These different modules are used within three different types of plants – summarized in Tab. 2.2 – for the production rsp. the storage of chemicals.

Tab. 2.2 Different infrastructure processes for the production / storage of chemicals established within this study

Name	Location	Unit	Comment
Liquid storage tank, chemicals, organics	CH	unit	This module represents typical tank facility for the storage of liquid chemicals. The module includes the land use (transformation, occupation) of the construction, the operational and the dismantling phase, the materials for used for the construction and maintain of the tanks and the buildings.
Storage building, chemicals, solid	CH	unit	This module represents a storage building for the storage of solid chemicals. The module includes the land use (transformation, occupation) of the construction, the operational and the dismantling phase, as well as the buildings.
Chemical plant, organics	RER	unit	This module represents an average chemical plant for the production of organic chemicals. The module includes the land use (transformation, occupation) of the construction, the operational and the dismantling phase, the facilities (incl. their dismantling) and the buildings.

For the regional storage of liquid chemicals storage tanks are used. In order to include the infrastructure of such tanks the module “liquid storage tank, chemicals, organics” was introduced. The regional storage of bulk chemicals uses often storage halls. In order to include the infrastructure of such regional storage the module “storage building, chemicals, solid” was introduced (see chapter 2.4 and

2.5). In cases where no information about the production site was available, the proxy module “chemical plant, organics” has been used. It is described in chapter 2.6.

In Fig. 2.1, the interrelations between the modules from Tab. 2.1 and Tab. 2.2 are shown. However, if detailed information about the infrastructure for a certain process or product is available, this information can be used to model the process more accurately.

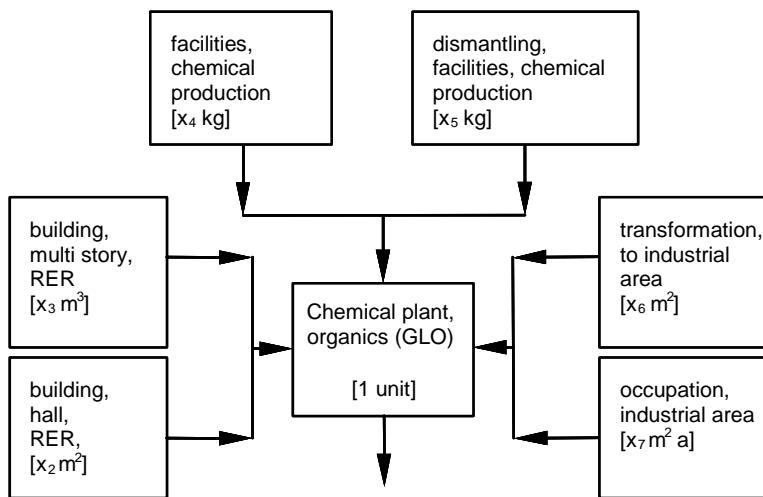


Fig. 2.1 Example of inventoring the infrastructure for the production of 1 kg of a chemical

The building and its land use are included in the modules in ecoinvent describing large industrial furnaces which are usually located in separate buildings. If one of them is used for the process heat, the total infrastructure for the furnace including buildings and land use must not be considered again to avoid double counting. In these cases, the land use and the area of „building, hall“ for the heat module is subtracted from the respective data of the chemical production plant.

2.1 Facilities, chemical production

The composition of the facilities of a chemical plant is varying much in function of the chemicals produced in the respective plant - therefore this facilities module here can be not more than a rough estimate. In European Commission 2001 a chemical production process is divided into five different steps (Raw material supply and preparation - synthesis - product separation and refinement - product handling and storage - emission abatement). This module here covers all these steps.

2.1.1 Process data

In KAM 2001 there is an example for the weight distribution between pipes (incl. supporting structure) and unit operation infrastructure. Similar information can be calculated, based on information of BASF¹. Tab. 2.3 summarizes all this information and shows the values used in this study.

¹ Personal communication from R. Wittlinger & K-H. Fischer, BASF Ludwigshafen, 19. September 2002

Tab. 2.3 Weight of unit operation installations (including storage facilities and pipes)

		KAM	BASF	this study
Unit operations	t	1200	5700	4000
Storage (educt, product)	t	n.a.	incl.	incl.
Pipes	km	24	8	16

In Jungbluth 2007 the material amount and the construction efforts of a distillation unit is shown as base for the calculation of the infrastructure of a refinery. In fact, European Commission 2001 shows, that the distillation unit is the most frequently used unit operation within the production of a big variety of organic chemicals. Its data are therefore taken as basis for the estimation of the composition of the whole unit operation infrastructure (incl. storage facilities) in this study.

Concerning the efforts for the manufacturing and installation of the different parts, only information about the production of the distillation unit is available from the above mentioned reference. Accordingly to the infrastructure, we assume again, that these data are representative for the all unit operations infrastructure. For the installation efforts of the pipes, we assume due to a lack of respective data half the amount from the distillation unit per kg of pipes.

Furthermore, we assume that the control units (electronic equipment) have about 5% of the weight of the total unit operation infrastructure. Tab. 2.4 summarizes the composition of the different parts of the facilities and the respective production efforts. Concerning the electronics equipment, its production and composition is described in detail in chapter **Fehler! Verweisquelle konnte nicht gefunden werden..**

Tab. 2.4 material composition and production efforts of the different parts of a chemical facility

	Unit Installations	pipes	supports for pipes	control unit	Total	amount per kg
Material composition						
Total weight	t	4000 [C]	393 [C]	63 [C]	200 [C]	4656
steel	t	1661 [A]	262 [B]	45 [D]	-	1969
chromium steel	t	1022 [A]	131 [B]	5 [D]	-	1158
rock wll	t	38 [A]	-	-	-	38
concrete	t	1278 [A]	-	13 [D]	-	1291
electronics	t	-	-	-	200 [C]	200
Production efforts						
Electricity	TJ	92 [A]	5 [C]	1 [C]	-	97
light fuel oil	TJ	21 [A]	1 [C]	0 [C]	-	22
water	m3	222364 [A]	10933 [C]	1751 [C]	-	235048
chemicals, inorganic	t	253 [A]	12 [C]	2 [C]	-	267
brazing solder, Cd-free	t	218 [A]	11 [C]	2 [C]	-	230

*) Data source: [A]: Jungbluth 2007, [B]: KAM 2001, [C]: assumptions according to text, [D]: assumption, based on information in KAM 2001

Concerning the transport of the different parts / materials to the chemical plant site, we use due to a lack of data, an estimated transport distance of 1000 km by lorry. Per kg of facilities this is equal to 1 tkm. The distance is estimated so huge due to the fact that there are only a few companies in Europe, producing such installations.

2.1.2 Data quality considerations

As already mentioned, this dataset is just a rough estimation. The total weight is based on two sources – showing already a high variation. Due to the fact that most material data originate from a distillation unit, the data have a high uncertainty concerning the technological correlation. This may also affect

the materials used. In general this infrastructure module has a high uncertainty and should only be seen as an approximation of the infrastructure of chemical facilities.

The resulting data together with their respective uncertainty values for the dataset „facilities, chemical production“ are shown in Tab. 2.5.

Tab. 2.5 In- / Outputs and uncertainty information for the dataset “facilities, chemical production”

	3702	3703	3706	3707	3708	3709	3792
	Name	Location	Unit	facilities, chemical production	UncertaintyType	StandardDeviation95 %	GeneralComment
	Location InfrastructureProcess Unit			RER 1 kg			
Ressource Input from Technosphere	Water, unspecified natural origin		m3	5.05E-02	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
	steel, low-alloyed, at plant	RER	kg	4.23E-01	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
	chromium steel 18/8, at plant	RER	kg	2.49E-01	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
	brazing solder, cadmium free, at plant	RER	kg	4.94E-02	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
	chemicals inorganic, at plant	GLO	kg	5.74E-02	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
	rock wool, at plant	CH	kg	8.23E-03	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
	concrete, sole plate and foundation, at plant	CH	m3	1.16E-04	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
	electronics for control units	RER	kg	4.30E-02	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	5.78E+00	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
	heat, light fuel oil, at industrial furnace 1MW	RER	MJ	4.77E+00	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature
Output Air emissions	transport, lorry 32t	RER	tkm	1	1	2.09	(4.n.a.n.a.n.a.n.a); standard distances
	facilities, chemical production	RER	kg	1			
Output Air emissions	Heat, waste		MJ	2.08E+01	1	1.4	(4.5,1,1,3,4); Estimate, mainly from Literature

2.2 Electronics for control units

2.2.1 System characterisation

These datasets here describe a typical composition of the equipment for operation/control of technical processes as well as its final disposal.

Each industrial device (paper machine, distillation column, etc.) has an electrical control unit that is used in order to operate such a device. The main components of such a control unit are (i) the electronic parts (usually some mounted PWB), (ii) cables (internal, but also for relying the control unit to the device) and, (iii) the housing around the whole unit. The dataset here distinguishes between these various parts. In a separate dataset, the dismantling and disposal activities are summed up.

The meta information for these datasets can be found in Tab. 2.6.

2.2.2 Dataset “electronics for control units”

Life Cycle Inventory

In Frischknecht et al. 1996 an average composition of electronic equipment for energy installations (photovoltaic) is described as: 14% printed wiring board (PWB), 8% cables, 46% steel (housing, etc.) and 32% HDPE. Due to a lack of other information, this composition is used in this study for electronics for control units. For the amount of cables it is assumed that 40% are internal cables, 10% the power consumption cable and 50% cables for the connection with the devices that are operated by this control unit. The respective plugs are disregarded here.

More details about the so determined composition, together with the used ecoinvent datasets, are summarized in Tab. 2.7.

Tab. 2.6 Ecoinvent meta information for the datasets of the power supply unit for Desktop PC within the database.

Name	electronics for control units	disposal, electronics for control units
Location	GLO	GLO
Infrastructure Process	1	1
Unit	kg	kg
Dataset Version	2.0	2.0
Included Processes	This module includes the composition of a typical control unit for devices in the industry. Included are the materials of the different components (housing, cables, mounted PWB). Process efforts are included for the treatment of metals and plastics only.	This module includes the dismantling of the electronic control equipment. The included processes are: transport to dismantling site and dismantling. The further treatment itself is not part of this dataset here.
Amount	1	1
Local Name	Elektronik für technische Anlagen	Entsorgung, Elektronik für Steuerung
Synonyms		
General Comment	The control unit has a composition of 46% steel (housing), 32% plastics, 14% printed wiring boards and 8% cables (various types).	The dismantled control unit has a composition of 46% steel (housing), 32% plastics, 14% printed wiring boards and 8% cables (various types).
Start Date	1990	1990
End Date	2005	2005
Data valid for entire period	1	1
Geography Text	Data used has no specific geographical origin (literature values).	Data used has no specific geographical origin (literature values).
Technology Text	estimated composition of the electronics for control units in the industry, based on literature	manual dismantling of the electronics for control units, assuming that big metal pieces are recycled, big plastic parts incinerated, and that cables and PWB are recycled through further treatment steps.
Representativeness	-	-
Production Volume	Unknown	Unknown
Sampling Procedure	own estimations & literature	own estimations & literature
Extrapolations	see Geography and Technology	see Geography and Technology
Uncertainty Adjustments	None	None

Tab. 2.7 Material specification of the dataset “electronics for control unit” (data sources: see text)

		Electronics control unit	Used ecoinvent dataset
		kg	
Housing, metal part	g	4.60E+02	steel, low-alloyed, at plant / sheet rolling
Housing, plastic part	g	3.22E+02	polyethylene, HDPE, at plant ¹⁾
cables, internal	g	3.20E+01	cable, ribbon cable, 20-pin, with plugs, at plant
cables, power supply	m	1.23E-01	cable, connector for computer, without plugs, at plant
cables, external	m	1.11E+00	cable, network cable, category 5, without plugs, at plant
PWB, mounted	g	1.40E+02	printed wiring board, mixed mounted, unspec., solder mix, at plant

¹⁾ including losses due to injection moulding process

Concerning the processes for the construction, the treatment of metals (by using the dataset for sheet rolling) resp. the treatment of plastics (by using the dataset for injection moulding) are taken into account. Further efforts towards the final equipment are due to lack of respective information not included here.

For the transport of all these materials to the production site of this control unit, we assume due to a lack of data, a total transport amount of 200 km by train and 100 km by lorry according to the methodology of ecoinvent (see Frischknecht et al. 2007).

As infrastructure, the module for the mounting of printed wiring boards (dataset “printed wiring board mounting plant”) is used as a proxy.

Data Uncertainty and Input Data for Database ecoinvent

The uncertainty scores established according to the method used in the ecoinvent project (see Frischknecht et al. 2007) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. The datasets represent a typical composition of the electronics used for control units of industrial devices, based on literature and own assumptions. Hence, the uncertainty values are estimated accordingly.

The resulting data together with their respective uncertainty values for the dataset „electronics for control units“ is shown in Tab. 2.8.

Tab. 2.8 In/outputs and uncertainty information for the dataset „electronics for control units“

Explanations	Name	Location	Infrastructure-Process	Unit	electronics for control units	uncertaintyType StandardDeviation 95%	GeneralComment	
							Location	Infrastructure-Process
							Unit	
Technosphere	steel, low-alloyed, at plant	RER	0	kg	4.60E-1	1	1.46	(3.5,4,1,3,5); approximation from 1 literature source
	sheet rolling, steel	RER	0	kg	4.60E-1	1	1.46	(3.5,4,1,3,5); approximation from 1 literature source
	polyethylene, HDPE, granulate, at plant	RER	0	kg	3.22E-1	1	1.46	(3.5,4,1,3,5); approximation from 1 literature source
	injection moulding	RER	0	kg	3.20E-1	1	1.46	(3.5,4,1,3,5); approximation from 1 literature source
	cable, ribbon cable, 20-pin, with plugs, at plant	GLO	0	kg	3.20E-2	1	1.46	(3.5,4,1,3,5); approximation from 1 literature source
	cable, connector for computer, without plugs, at plant	GLO	0	m	1.23E-1	1	1.46	(3.5,4,1,3,5); approximation from 1 literature source
	cable, network cable, category 5, without plugs, at plant	GLO	0	m	1.11E+0	1	1.46	(3.5,4,1,3,5); approximation from 1 literature source
	printed wiring board, mounted, unspecified, at plant	GLO	0	kg	1.40E-1	1	1.46	(3.5,4,1,3,5); approximation from 1 literature source
	transport, lorry>16t, fleet average	RER	0	tkm	1.00E-1	1	2.09	(4,5,na,na,na,na); standard distances
	transport, freight, rail	RER	0	tkm	2.00E-1	1	2.09	(4,5,na,na,na,na); standard distances
Outputs	printed wiring board mounting plant	GLO	1	unit	2.08E-7	1	3.77	(4,5,1,3,5,4); rough assumption
Outputs	electronics for control units	RER	0	kg	1.00E+0			

2.2.3 Dataset “disposal, electronics for control units”

Life Cycle Inventory

According to, Doka 2007 for the disposal of electronic equipment the following assumption can be made: Large metal parts (housing, cooling sheets, etc.) can be separated and recycled; most bigger plastic parts (without the printed wiring board) can be separated and are incinerated in a MSWI; printed wiring boards are separated and recycled in a copper smelters (more details – see Doka 2007). The electricity consumption for the dismantling is in the order of 20 to 110 kWh/t of electronic input. Based on this information, the dismantling of the control units is calculated within this study as following:

- **Transport to dismantling facility:** For the transport of the whole control unit to the dismantling facility, an average distance of 100 km (100% lorry) is assumed. This is based on the fact, that within Switzerland - and due to the WEEE soon also in Europe - quite a close network of dismantling companies for electronic scrap exists.
- **(manual) Dismantling of the control unit:** It is assumed that the first dismantling steps are manual steps – hence, no big energy amounts (apart from the electricity for an electric screw driver) are used in this step. Due to a lack of more precise information, no energy consumption is thus taken into account for this step here. The control unit is dismantled into the following fractions in this step: large metal parts (46%), large plastic parts (32%), cables (8%) and PWB (14%).
- **Further treatment of the different compounds:** For the further treatment of the different fractions, the following processes and modules from ecoinvent are used:
 - **Large metal parts:** These parts go for recycling to the steel industry. Therefore only the transport has to be considered in this process step – further environmental loads are due to the used cut-off rules (see Frischknecht et al. 2007) not part of this process step. For this, a distance of 500 km is assumed, 40% by train and 60% by lorry.
 - **Large plastic parts:** These parts are incinerated. Therefore, the module "disposal, plastics, industrial electronics, 15.3% water, to municipal incineration" is used. Additionally, the transport from the dismantling site to the incineration has to be considered. As there are quite a lot of such incineration plants in Switzerland, a distance of 100 km by lorry is assumed.
 - **Cables:** The further treatment of cables from electric and electronic devices is described in the dataset “disposal, treatment of cables”. Hence this dataset is used here. The transport to this further treatment is already included in the mentioned module - therefore, no transport is accounted for in this module here.
 - **PWB:** The further treatment of PWB from electric and electronic devices is described in the dataset “disposal, treatment of printed wiring boards”. Hence this dataset is used here. The transport to this further treatment is already included in the mentioned module - therefore, no transport is accounted for in this module here.

Data Uncertainty and Input Data for Database ecoinvent

The uncertainty scores established according to the method used in the ecoinvent project (see Frischknecht et al. 2007) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. The datasets represent a rough estimation of the dismantling activities for the control units of industrial devices, based on literature and own assumptions. Hence, the uncertainty values are estimated accordingly.

The resulting data together with their respective uncertainty values for the dataset „disposal, electronics for control units“ is shown in Tab. 2.9.

Tab. 2.9 In-/outputs and uncertainty information for the dataset „disposal, electronics for control units“

Explanations	Name	Location	Infrastructure-Process	Unit	disposal, electronics for control units	uncertaintyType	StandardDeviation 95%	GeneralComment	
								RER	0
								kg	
Technosphere	transport, lorry32t	RER	0	tkm	2.70E-1	1	2.80	(4,5,1,3,5,5); rough assumption	
	transport, freight, rail	RER	0	tkm	9.20E-2	1	2.80	(4,5,1,3,5,5); rough assumption	
	road vehicle plant	RER	1	unit					
	disposal, plastic, industr. electronics, 15.3% water, to municipal in	CH	0	kg	3.20E-1	1	1.21	(4,na,na,na,na,na); based on composition of this device	
	disposal, treatment of cables	GLO	0	kg	8.00E-2	1	1.21	(4,na,na,na,na,na); based on composition of this device	
	disposal, treatment of printed wiring boards	GLO	0	kg	1.40E-1	1	1.21	(4,na,na,na,na,na); based on composition of this device	
Outputs	disposal, electronics for control units	RER	0	kg	1.00E+0				

2.3 Disposal, facilities, chemical production

Like the composition of the facilities of a chemical plant is varying much in function of the chemicals produced in the respective plant – the dismantling depends much from the produced chemicals and therefore can vary much. Therefore, this module can only be a very rough estimation.

2.3.1 Process data

For the different parts of the facility no specific information was available – therefore the following assumptions are used here for the different parts of the facilities (according to Tab. 2.4):

- **Unit installations:** While for concrete it is assumed that 50% are recycled (expressed by the module „Disposal, building, concrete, not reinforced, to recycling“) and 50% go to final disposal (module “Disposal, building, concrete, not reinforced, to final disposal”), rock wool goes completely to final disposal (module “Disposal, building, mineral wool, to final disposal”). For the metals it is assumed that due to contamination, only 50% of the different steel types can be recycled, while the other 50% go to a landfill (module “disposal, steel, 0% water, to inert material landfill”).
- **Pipes and supports:** It is assumed that steel can be recycled completely while concrete is assumed to be 50% recycled (module „Disposal, building, concrete, not reinforced, to recycling“) and 50% to final disposal (module “Disposal, building, concrete, not reinforced, to final disposal”).
- **Control unit:** The detailed dismantling of electronics is described in chapter 2.2.3 - its resulting module is used for the control unit of the chemical facilities.
- **Transport:** While for concrete and rock wool, all transport amounts are included in the following disposal modules, for metals the respective transport amount from the dismantling of the facilities until the recycler, rsp. the landfill of 100 km by lorry is included into this module.

2.3.2 Data quality considerations

The whole module is based on estimations of the author of this part of the study - therefore, the uncertainty is high. All in all, also this is a dataset that represents not more than a rough estimation. The resulting data together with their respective uncertainty values for the dataset „disposal, facilities, chemical production“ is shown in Tab. 2.10.

Tab. 2.10 In-/outputs and uncertainty information for the dataset „disposal, facilities, chemical production“

	3702 Name	Location	Unit	3703	3706	3707 <i>disposal, facilities, chemical production</i>	3708	3709	3792
						<i>RER 1 kg</i>			
Technosphere Waste	transport, lorry 32t		RER	tkm	6.70E-02	1	2.09	(4,n.a,1,n.a,n.a); estimation, based on assumptions (5.n.a,n.a,n.a,n.a); rough estimation (5.n.a,n.a,n.a,n.a); rough estimation (5.n.a,n.a,n.a,n.a); rough estimation (5.n.a,n.a,n.a,n.a); rough estimation (5.n.a,n.a,n.a,n.a); rough estimation	
	disposal, building, concrete, not reinforced, to final disposal								
	disposal, building, concrete, not reinforced, to sorting plant								
	disposal, steel, 0% water, to inert material landfill								
	disposal, electronics for control units								
	disposal, building, mineral wool, to final disposal								
Output	disposal, facilities, chemical production		RER	kg	8.23E-03	1	1.5	(5.n.a,n.a,n.a,n.a); rough estimation	

2.4 Liquid storage tank, chemicals, organics

2.4.1 Process

The infrastructure of the liquid storage tank was estimated with help of data from fuel storage tanks. The storage tank infrastructure for organic chemicals assessed in this inventory includes a storage volume of 16'000 m³ (4 tanks with 4000 m³ volume each). Besides the land use and the materials such as steel, concrete, bitumen and paint, also transport of all the materials to the construction site needed to be estimated. The energy used during the construction itself was neglected. Concerning the dismantling and the waste processes, no contamination of the disposed material was considered. Transport and the energy demand for dismantling was included in the used disposal processes. The construction of the storage tanks refers to the storage of organic chemicals and, therefore, no coating or plating of the inner tank wall of the tank was considered.

2.4.2 Land use and used processes

Land use

The land use was calculated from 3 smaller storage tank sites in Basel with a total storage volume between 10'000 m³ and 84'000 m³ (Portofbasel 2002). In average a land use of 0.138 m² m⁻³ was calculated. For the storage volume of 16'000 m³ as assessed in this module a total area of 2200 m² was used. For the time of occupation 50 years were assumed. Further 2 years of occupation as construction site for construction and dismantling were assumed. The occupation of the area before the occupation as industrial area is not known (transformation from unknown). Depending on the actual site conditions the land use may vary. For a large fuel storage tank farm a land use of 0.286 m² m⁻³ was calculated (Monopol Colors 2002). The minimum possible land use for the tank will be around 0.064 m² m⁻³. The calculated values for the occupation and transformation of the whole site and per kg of product used in this inventory are given in Tab. 2.11.

Construction materials

The amount of steel used for the construction of fuel storage tanks lies according to Frischknecht et al. 1996 at 18-24 kg m⁻³ storage volume. From data of the dismantling of a tank site with 45 tanks in Germany with 617'000 m³ total storage volume, a steel amount of 26 kg m⁻³ storage volume was calculated (WALTER BAU 2002). For smaller tanks (820 m³) the amount of steel increases to 38 kg m⁻³ storage volume (graysonline 2000). For this inventory the value of 26 kg m⁻³ storage volume was used, which leads to a total amount of 416 t steel (low alloyed). For the painting of the outer tank wall a total wall area of 5300 m² and a total coating thickness of 0.18 mm was assumed (WALTER BAU 2002). It was assumed that the life time of the tank will be 50 years and during this time the paint will

be renewed 3 times. With these assumptions an amount of 2.86 m³ or 4 t paint (approximated with alkyd varnish 60% in solvent with an assumed density of 1.4 kg m⁻³) is needed during the life time of the tank for coating.

For safety reasons the tanks are often surrounded by a concrete wall of about 4 m height. The thickness of the concrete wall was assumed to be 0.3 m as for regional storage of fuel in Frischknecht et al. 1996. The same thickness was applied for the concrete used for the floor. With the assumed average land occupation of 2200 m² an amount of concrete of 885 m³ was calculated for the whole site (660 m³ for the floor and 225 m³ for the walls). The value used in Frischknecht et al. 1996 (200 kg m⁻³ storage volume or 1455 m³ for the whole site) seemed too high and therefore the calculated value was taken for this inventory. A coating with a bitumen thickness of 5 cm as in Frischknecht et al. 1996 was assumed for floor coating. This leads to a total amount of 110 t bitumen for the coating of the 2200 m² floor area. For the 225 m³ concrete used for the walls a reinforcement with 1.5 vol.-% steel was assumed. This leads to an additional steel demand of 26 t (reinforcing steel).

Transport of building materials

For the transport of the building materials to the construction site the standard distances were used. For bitumen and paint the values given for plastics was used (200 km rail, 50 km road). This leads to a transport demand of 22.1 * 10³ tkm road and 265.2 * 10³ tkm rail for steel, 5.8 * 10³ tkm road and 23.3 * 10³ tkm rail for bitumen and paint, and 38.9 * 10³ tkm road for concrete. For the road transport a 28 t lorry was used.

Disposal building infrastructure

For the dismantling of the storage tanks the disposal modules for buildings was used. Those processes were applied to the corresponding amount of concrete, steel, bitumen and paint.

Emissions

In the application of the paint for coating the tank surface (4 t paint, approximated with alkyd varnish 60% in solvent) the solvent will emit which is accounted as 2.7 t NMVOC emissions to air.

Tab. 2.11 Land use and used processes for liquid storage tank, chemicals, organics.

Process, construction, disposal, emissions	Unit	per Unit¹	per m³ of product²
Concrete, sole plate and foundation, at plant	m ³	885	184 * 10 ⁻⁶
Reinforcing steel, at plant	kg	26 * 10 ³	5.42 * 10 ⁻³
Steel, low-alloyed, at plant	kg	416 * 10 ³	86.7 * 10 ⁻³
Alkyd varnish, 60% in solvent, at plant	kg	4 * 10 ³	0.83 * 10 ⁻³
Bitumen, at refinery	kg	110 * 10 ³	22.9 * 10 ⁻³
Transport, lorry 28t	tkm	67 * 10 ³	14 * 10 ⁻³
Transport, freight, rail	tkm	289 * 10 ³	60 * 10 ⁻³
NMVOC, non-methane volatile organic compounds, unspecified origin, low population density	kg	2.7 * 10 ³	0.55 * 10 ⁻³
Disposal, building, bulk iron (excluding reinforcement), to sorting plant	kg	416 * 10 ³	86.7 * 10 ⁻³
Disposal, building, concrete, not reinforced, to final disposal	kg	1.45 * 10 ⁶	302 * 10 ⁻³
Disposal, building, reinforced concrete, to final disposal	kg	521 * 10 ³	109 * 10 ⁻³
Disposal, building, paint on metal, to final disposal	kg	4 * 10 ³	0.83 * 10 ⁻³
Disposal, building, bitumen sheet, to final disposal	kg	110 * 10 ³	22.9 * 10 ⁻³
Transformation, from unknown	m ²	2.2 * 10 ³	458 * 10 ⁻⁶
Transformation, to industrial area, built up	m ²	2.2 * 10 ³	458 * 10 ⁻⁶
Transformation, from industrial area, built up	m ²	2.2 * 10 ³	458 * 10 ⁻⁶
Occupation, industrial area, built up	m ² a	110 * 10 ³	22.9 * 10 ⁻³
Occupation, construction site	m ² a	4.4 * 10 ³	0.92 * 10 ⁻³

¹Liquid storage tank for organic chemicals with a storage volume of 16'000 m³ (4 tanks with 4'000 m³)

²Calculated for a product throughput of 96'000 m³ per year during the whole lifetime (50 years) of the site. Per m³ stored product therefore a share of 208 * 10⁻⁹ units of the infrastructure is needed.

2.4.3 Data quality considerations

Tab. 2.12 shows the data quality indicators for the inventory of the regional storage infrastructure for organic chemicals. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Due to the fact that most data origins from the storage of fuels, there is high uncertainty in the technological correlation. This may also affect the materials used for the tank wall. Also high uncertainties occur within the disposal of the tanks after use because processes for buildings were used as approximation and no contamination of the materials was included. In general this infrastructure module has a high uncertainty and should only be seen as an approximation of the infrastructure for the regional storage of liquid chemicals.

Tab. 2.12 In- / Outputs for the module “liquid storage tank, chemicals, organics”, location CH

Process output: 1 unit, liquid storage tank, chemicals, organics, CH		Value	Unit	Uncertainty			Comment
Name, Location	Type			Score	St.Dev.		
From technosphere	concrete, sole plate and foundation, at plant, CH	8.55E+2	m3	lognorm	5.5,2,1,4,5	1.88	Estimation based on theoretical calculation
	reinforcing steel, at plant, RER	2.60E+4	kg	lognorm	5.5,2,1,4,5	1.88	Estimation based on theoretical calculation
	steel, low-alloyed, at plant, RER	4.16E+5	kg	lognorm	3.5,2,1,3,5	1.40	Based on data for fuel storage
	alkyd paint, white, 60% in solvent, at plant, RER	4.00E+3	kg	lognorm	4.5,2,1,4,5	1.68	Estimation based on data for fuel storage
	bitumen, at refinery, CH	1.10E+5	kg	lognorm	4.5,2,1,4,5	1.68	Estimation based on data for fuel storage
	transport, freight, rail, CH	2.89E+5	tkm	lognorm	4.5,nA,nA,nA,nA	2.09	Estimated with standard distances for Switzerland
	transport, lorry 28t, CH	6.70E+4	tkm	lognorm	4.5,nA,nA,nA,nA	2.09	Estimated with standard distances for Switzerland
	disposal, building, bulk iron (excluding reinforcement), to sorting plant, CH	4.16E+5	kg	lognorm	4.5,2,1,4,5	1.68	Same amount as for material input
	disposal, building, concrete, not reinforced, to final disposal, CH	1.45E+6	kg	lognorm	4.5,2,1,4,5	1.68	Same amount as for material input
	disposal, building, reinforced concrete, to final disposal, CH	5.21E+5	kg	lognorm	4.5,2,1,4,5	1.68	Same amount as for material input
Resources	disposal, building, paint on metal, to final disposal, CH	4.00E+3	kg	lognorm	4.5,2,1,4,5	1.68	Same amount as for material input
	disposal, building, bitumen sheet, to final disposal, CH	1.10E+5	kg	lognorm	4.5,2,1,4,5	1.68	Same amount as for material input
	Transformation, from unknown	2.20E+3	m2	lognorm	4.5,2,1,4,5	1.93	Based on data for fuel storage
	Transformation, to industrial area, built up	2.20E+3	m2	lognorm	4.5,2,1,4,5	1.93	Based on data for fuel storage
Occupation	Occupation, industrial area, built up	1.10E+5	m2a	lognorm	4.5,2,1,4,5	2.37	Based on data for fuel storage and estimates
	Occupation, construction site	4.40E+3	m2a	lognorm	4.5,2,1,4,5	2.37	Based on data for fuel storage and estimates
	(=) NMVOC, non-methane volatile organic compounds, unspecified origin, air, low population density	2.70E+0	kg	lognorm	4.5,2,1,5,5	2.80	Estimated from data for fuel storage tanks
1) Emissions							

2.5 Storage building, chemicals, solid

2.5.1 Process

The infrastructure of the storage building for solid chemicals was estimated with help of data from storage buildings used for sodium chloride storage in Switzerland. The storage site assessed contains two building halls and a total floor area of about 6'000 m². In those buildings 38'000 t of salt (about 30 * 10³ m³) are stored. The production capacity of the adjacent plant is 230'000 t per year (Schweizer Rheinsalinen 1998). This leads to an average storage time of two month assuming that all material is stored before shipping. Besides land use and construction, also the disposal of the building was considered. For the dismantling and the waste processes no contamination of the disposed material was considered. The construction of the storage hall refers to the storage of bulk chemicals, which need no special caution for storage due to toxic effects or material properties.

2.5.2 Land use and used processes

Land use

Concerning land use, besides the estimated 6'000 m² building floor area additional 3'000 m² were considered as service area for lorry traffic and loading. The whole area was assumed to be sealed. For the time of occupation 50 years were assumed. Further two years of occupation as construction site for construction and dismantling were assumed. The occupation of the area before the occupation as industrial area is not known (transformation from unknown). Depending on the actual site conditions and product the land use may vary largely. The calculated values for the occupation and transformation of the whole site and an estimation per kg of product used in this inventory are given in Tab. 2.13.

Building infrastructure

According to photos in Schweizer Rheinsalinen 1998, the height of the building hall was estimated to be about 15 m. Due to the fact that the building hall in the inventory “building, hall, CH” is only 7 m high, the double floor area was used to assess the amount of building materials. This leads to an overestimate of the roof area in this inventory. With these assumptions 12'000 m² of building hall area was calculated for this inventory. In this building module the disposal of the building is already included but no land use. No further materials were considered.

Tab. 2.13 Land use and used processes for storage building, chemicals, solid.

Resource, Use	Unit	per Unit ¹	per m ³ of product ²
Building, hall	m ²	12 * 10 ³	1.33 * 10 ⁻³
Occupation, industrial area, built up	m ² a	450 * 10 ³	50 * 10 ⁻³
Occupation, construction site	m ² a	18 * 10 ³	2 * 10 ⁻³
Transformation, from unknown	m ²	9 * 10 ³	1 * 10 ⁻³
Transformation, to industrial area, built up	m ²	9 * 10 ³	1 * 10 ⁻³
Transformation, from industrial area, built up	m ²	9 * 10 ³	1 * 10 ⁻³

¹ Bulk storage for chemicals with a storage volume of 38'000 t or 30'000 m³ (in 2 halls)² Calculated for a product throughput of 0.23 Mt or 180'000 m³ per year during the whole lifetime (50 years) of the site. Per m³ stored product therefore a share of 111 * 10⁻⁹ units of the infrastructure is needed.

2.5.3 Data quality considerations

Tab. 2.14 shows the data quality indicators for the inventory of the regional storage infrastructure for bulk chemicals. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation, and sample size. Due to the fact that the data was estimated only from one storage site for salt production, there is a high uncertainty in the technological correlation. In general this infrastructure module has a high uncertainty and should only be seen as an approximation of the infrastructure for the regional bulk chemical storage.

Tab. 2.14 In- / outputs for the module “storage building, chemicals, solid”, location CH

Resources	Process output: 1 unit, storage building, chemicals, solid, CH	Uncertainty			Comment		
		Type	Score	St.Dev.			
	1) building, hall, CH	1.20E+4	m2	lognorm	4,5,1,2,4,5	1.68	Estimated with data from 1 site
	Transformation, from unknown	9.00E+3	m2	lognorm	4,5,1,1,4,5	1.92	Estimated with data from 1 site
	Transformation, to industrial area, built up	9.00E+3	m2	lognorm	4,5,1,1,4,5	1.92	Estimated with data from 1 site
	Transformation, from industrial area, built up	9.00E+3	m2	lognorm	4,5,1,1,4,5	1.92	Estimated with data from 1 site
	Transformation, to unknown	9.00E+3	m2	lognorm	4,5,1,1,4,5	1.92	Estimated with data from 1 site
	Occupation, industrial area, built up	4.50E+5	m2a	lognorm	4,5,1,1,4,5	2.37	Estimated with data from 1 site
	Occupation, construction site	1.80E+4	m2a	lognorm	4,5,1,1,4,5	2.37	Estimated with data from 1 site
	1) From technosphere						

2.6 Chemical plant, organics

For the infrastructure of the chemical production plant modules for the construction and dismantling of the buildings and the chemical equipment was used. Further the land use of the plant is also included. In the module no emissions or wastes from contamination with chemicals is included. The process chain was assessed as shown in Fig. 2.2.

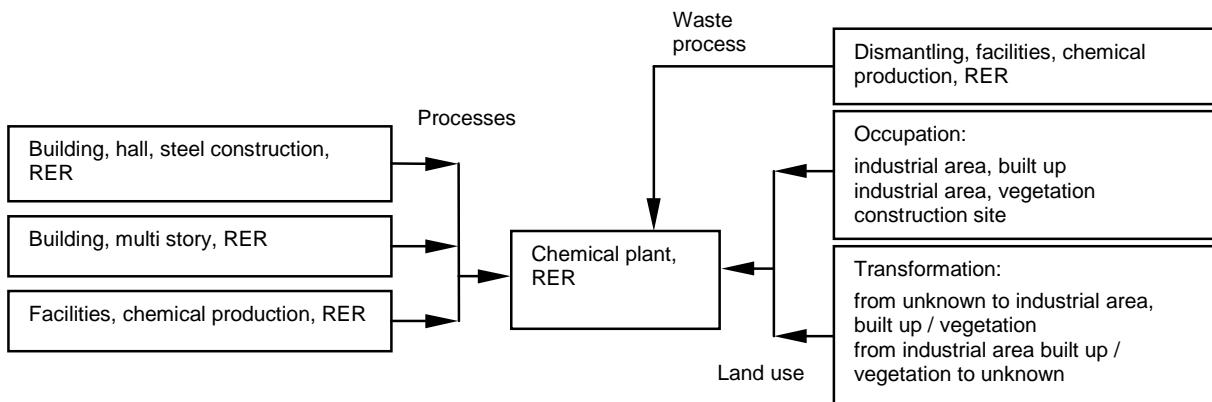


Fig. 2.2 Process chain for the infrastructure of a chemical plant

The infrastructure of the chemical plant was assessed using data from the chemical plant sites in Gendorf (Germany) and from the BASF site of Ludwigshafen (Germany). On the Gendorf site 12 companies produce 1500 different end products with a total amount 1.25 Mt each year. If intermediates are also included the amount of products rises to 2.05 Mt a⁻¹ (Gendorf 2000). The largest company on the site is Clariant with a share of 58% of the total product output (including intermediates). The production includes ethylene glycol, glycol ether, intermediates produced from ethylene oxide. The second large producer on the site is Vinnolit GmbH with a share of 37% of the total product output. Vinnolit produces besides chlorine, 1,2-dichloroethane and vinyl chloride also to a smaller amount PVC plastics.

On the other examined site – BASF Ludwigshafen – about 8000 different end products with a total amount of 9.1 Mt per year are produced (BASF 2001). The whole site is owned by the same company.

The production in both examined sites cover many different (mainly organic) chemical processes and they were chosen therefore as base for an inventory of the infrastructure of chemical processes. Due to the high variability of production processes this infrastructure inventory, nevertheless, can only be used as a rough estimation for chemical processes where no other data is available.

2.6.1 Land use and used processes

Land use

The relevant mass for this study is not the total land use of such a chemical complex due to the fact that it sorts a huge amount of different products, but the land use for one production unit (that still can produce several different chemicals) within such a complex. While for the BASF site, the number of production units is given by the owner, for the Gendorf site – based on information in the environmental statement (Gendorf 2000) – we estimate about 20 production units, producing chemical products. Based on this information, the average land use for one single production unit can be calculated. Tab. 2.15 summarises the data used and the result achieved.

Tab. 2.15 Land use of a chemical plant (data from BASF 2001; Gendorf 2000)

	Gendorf	BASF	This project
Land use, total [ha]	230	711	
Land use, built [ha]	115	640 ¹	
Production volume [Mt]	1.25	9.11	
No. of production units	20 ²	250	
Land use per production unit (built area) [ha]	5.8	2.6	4.2
Sold products per production unit [Mt/a]	0.06	0.04	0.05
Specific land use (built area) [$m^2 / (t/a)$]	0.9	0.7	0.8
Specific land use (unoccupied area) [$m^2 / (t/a)$]	0.9	0.07	0.25

¹ estimation, based on the air photographie of BASF site Ludwigshafen

² estimation, based on Gendorf 2000

While for the land use per production unit quite big differences are visible between the two chemical complexes, the amount of sold product as well as the specific land use are very close to each other. Further data from Atofina show a big variety concerning the specific land-use in function of the produced chemicals – ranging from $0.15 m^2$ per t of yearly production for a hydrogen peroxide production plant (ATOFINA 2000b) up to $3.4 m^2$ per t of yearly production for the production of glues (ATOFINA 2000a). For this study, the value calculated in Tab. 2.15 is used, as the module is dedicated primary for basic chemicals. The occupation of the area before the occupation as industrial area is not known (transformation from unknown). Depending on the actual site conditions and production process the land use may vary largely.

For the total land use the variations are even larger due to surrounding lands belonging to the plant which can be large in low populated areas. The two sites examined are a typical example – while the BASF site in Ludwigshafen is situated within the town, the other site is situated in a more rural area – therefore having more space. This fact can also be seen in the last line of Tab. 2.15. For this study, we assume a specific unoccupied land-use of $0.25 m^2/(t/a)$, or 1.25 ha. Third parameter concerning land use is the time, that is used to construct and to dismantle the chemical plant. Therefore, we assume each time 1 year.

Building infrastructure

For the sites of Gendorf and BASF it was estimated with help of pictures that only around 50% of the built area is occupied by buildings. On the other area production equipment or tanks occupy the area (without surrounding building structure). Further it was assumed that the building infrastructure contains to 50% building halls and to 50% multiple story buildings with an average height of 15 m. With his assumptions 1.05 ha of building hall area and $1.58 * 10^5 m^3$ of multiple story building volume was calculated for the whole plant site. It was assumed that the life time of the buildings will be 50 years and therefore no replacement occurs during the assumed occupation time (production time). The final dismanteling of the buildings is already included into the used datasets.

Chemical production facilities

The estimation of the amount of production facilities is difficult and uncertain. Big players on the market for the construction of chemical plants (e.g Linde, Lurghi) were not able to give any informa-

tion concerning this question. According to information of BASF², the total weight of a production unit is about 5'700 t of installations (without foundations), almost 100% of it is some kind of steel. From data of a methanol plant (Pehnt 2002) an amount of 14'700 t for the production facilities can be deducted. In this case 90% of the weight was metal (mainly steel). Assuming that the remaining 10% are mainly the foundation, we can calculate for the production unit of BASF a total amount of 6'300 t including a similar foundation.

For this study, we use value from the BASF plant, means 6'300 t of production facilities, due to the fact that the BASF plant produces a mix of different chemicals and therefore this data are more representative for the various chemical products. For this equipment a life span of 25 years is assumed. Therefore within the assumed occupation time of 50 years the equipment will be replaced 2 times. Therefore a value of 12'600 t for the total equipment weight of the whole plant site is used in this study. For dismantling of the facilities, again the same amount of 12'600 t is used in this study. All transports are already included in the two modules.

2.6.2 Data quality considerations

As already mentioned, this dataset is just a rough estimation. The total weight is based on two sources – showing already a high variation. Due to the fact that most material data origins from a distillation unit, there is high uncertainty concerning the technological correlation. This may also affect the materials used. In general this infrastructure module has a high uncertainty and should only be seen as an approximation of the infrastructure of chemical facilities.

The resulting data together with their respective uncertainty values for the dataset „facilities, chemical production“ are shown in Tab. 2.16.

Tab. 2.16 Input data and uncertainty values for the dataset „chemical plant, organics“

Explanation	Name	Location	Unit	chemical plant, organics	RER 1 unit	UncertaintyType	StandardDeviation95%	GeneralComment	
								Location	
								InfrastructureProcess	
								Unit	
Resources	Transformation, from unknown	m2	5.45E+04	1	2.58	(4,3,1,3,4,4); estimated from two sites			
	Transformation, to industrial area, built up	m2	4.20E+04	1	2.58	(4,3,1,3,4,4); estimated from two sites			
	Transformation, to industrial area, vegetation	m2	1.25E+04	1	2.58	(4,3,1,3,4,4); estimated from two sites			
	Occupation, industrial area, built up	m2a	2.10E+06	1	2.15	(4,3,1,3,4,4); estimated from two sites			
	Occupation, industrial area, vegetation	m2a	6.25E+05	1	2.15	(4,3,1,3,4,4); estimated from two sites			
	Occupation, construction site	m2a	8.40E+04	1	2.15	(4,3,1,3,4,4); estimated from two sites			
	building, hall, steel construction	CH	1.05E+04	1	3.58	(4,3,1,3,4,4); estimated from two sites			
	building, multi-storey	RER	m3	1.58E+05	1	3.58	(4,3,1,3,4,4); estimated from two sites		
	facilities, chemical production	RER	kg	1.26E+07	1	3.58	(4,3,1,3,4,4); estimated from personal information		
	disposal, facilities, chemical production	RER	kg	1.26E+07	1	3.58	(4,3,1,3,4,4); estimated from personal information		
Output	chemical plant, organics	RER	unit	1					

² Personal communication from R. Wittlinger & K-H. Fischer, BASF Ludwigshafen, 19. September 2002

3 Energy for production of chemicals

3.1 Heat from unknown source

In case no information is available about the source of the heat energy needed in processes, the fuel mix of the average steam production in the European chemical industry according to Boustead 1999 is used. These data are the arithmetic average of all 215 steam plants that have been examined in the course of Boustead's work on chemicals and plastics.

The energy content of steam according to Boustead 1999 is 2.75 MJ/kg which corresponds to an overall efficiency of 74%. This factor is used to calculate the energy demand for the production of steam per MJ. (See Tab. 3.1)

Tab. 3.1 Gross energy in MJ required for producing on-site steam. (Boustead 1999)

Fuel type	Energy content of delivered fuel [MJ]			
	For 1 kg of steam Boustead 1999	For 1 kg of steam (this project)	For 1 MJ of steam (this project)	Comments
Coal	0.53	0.53	0.19	
Oil	0.78	0.78	0.28	
Gas	1.86	2.2	0.80	Incl. hydrogen
Hydro electricity	0.03	0.03	0.011	37.5%
Nuclear electricity	0.05	0.05	0.018	62.5%
Lignite	< 0.01	0	0.00	neglected
Biomass	< 0.01	0	0.00	neglected
Hydrogen	0.34	0	0.00	Included in gas
Recovered energy	0.13	0	0.00	Not inventoried
Unspecified	0.010	0	0.00	
Peat	< 0.01	0	0.00	neglected
Totals	3.72	3.6	1.31	

According to that, the process “heat, unspecific, in chemical plant” is defined. The ecoinvent meta information is given in Tab. 3.2 and the in- and outputs with their representation in ecoinvent are shown in Fig. 3.1.

Tab. 3.2 Meta data of unspecific heat production process

Name	heat, unspecific, in chemical plant
Location	RER
Infrastructure Process	0
Unit	MJ
Data Set Version	2.0
Included Processes	Includes the heat production needed for the production of 1 MJ (=0.3636 kg) steam from cold water. Does not include the water input because steam is often used in closed systems.
Amount	1
Local Name	Nutzwärme, unspezifisch, in Chemiewerk
Synonyms	steam//Dampf
General Comment to reference function	To be used for heat energy production in average chemical plant.
CAS Number	
Start Date	1989
End Date	1997
Data Valid For Entire Period	1
Other Period Text	
Geography text	Data from Europe
Technology text	Average technology in chemical and plastics industry in Europe
Representativeness [%]	
Production Volume	unknown
Sampling Procedure	Literature
Extrapolations	none

General Flow information				Representation in ecoinvent							Uncertainty			
Input	Process Name	Output	Remarks	Category	Sub category	Infrastructure	Location	Module name in ecoinvent	Mean value	Unit	Source mean value	Type	StDev 95%	General Comment
Coal	heat, unspecific, in chemical plant			hard coal	heating systems	No	RER	hard coal, burned in industrial furnace 1-10MW	1.93E-01	MJ	Boustead 1999	1	1.21	(1,2,2,1,3,1)
Oil	heat, unspecific, in chemical plant			oil	heating systems	No	RER	light fuel oil, burned in industrial furnace 1MW, non-modulating	2.84E-01	MJ	Boustead 1999	1	1.21	(1,2,2,1,3,1)
Gas	heat, unspecific, in chemical plant			natural gas	heating systems	No	RER	natural gas, burned in industrial furnace >100kW	8.00E-01	MJ	Boustead 1999	1	1.21	(1,2,2,1,3,1)
Hydro electricity	heat, unspecific, in chemical plant		as CH production mix (60% nuclear, 40% hydropower)	electricity	production mix	No	CH	electricity, medium voltage, production CH, at grid	3.03E-03	kWh	Boustead 1999	1	1.21	(1,2,2,1,3,1)
Nuclear electricity	heat, unspecific, in chemical plant		as CH production mix (60% nuclear, 40% hydropower)	electricity	production mix	No	CH	electricity, medium voltage, production CH, at grid	5.05E-03	kWh	Boustead 1999	1	1.21	(1,2,2,1,3,1)
	Process heat in chemical plant	steam = 2.75 MJ/kg or 2.4 MJ/kg (latter if condensed steam is reheated)	chemicals	organics	No	RER	heat, unspecific, in chemical plant	1.00E+00	MJ					

Fig. 3.1 In- and Output flows of "heat, unspecific, in chemical plant" and their representation in ecoinvent

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Part II

Inventoried Chemicals

Authors: see individual chapter

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Final report of the project of a National Life Cycle Inventory Database "Ecoinvent 2000" commissioned by BUWAL/BFE/ASTRA/BLW

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1 Acetaldehyde

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1.1 Introduction

Acetaldehyde (C_2H_4O , CAS N° 75-07-0) is a colorless liquid with a pungent, suffocating odor that is slightly fruity when diluted. Acetaldehyde is completely miscible with water and most organic solvents. The most important chemical and physical properties of acetaldehyde are given in Tab. 1.1.

Synonyms for acetaldehyde: acetic aldehyde, acetylaldehyde, aceteldehyde, aldehyde, ethanal, ethyl aldehyde.

Tab. 1.1 Chemical and physical properties of acetaldehyde (Taken from Chemfinder (2003)).

Property	Value	Unit	Property	Value	Unit
Molecular weight	44.053	$g\ mol^{-1}$	Melting point	-123.5	°C
Vapor Density	1.52	$g\ cm^{-3}$	Boiling point	20.1	°C

The following description of production technology and the use of acetaldehyde are summarised from Fleischmann 2000.

1.2 Reserves and Resources

Acetaldehyde is produced basically from ethylene. Therefore, the resources available as well as the reserves are the same as for this chemical, described in the corresponding chapter.

The worldwide production of acetaldehyde was 1993 1.35 Mio Tons, from what 0.6 Mio Tons correspond to Western Europe. The worldwide production has been nearly constant since the early 1980s, although in the USA the production of acetic acid from acetaldehyde ceased in 1991.

1.3 Production Technologies and Use

1.3.1 Production technologies for the production of acetaldehyde

Today the most important production process worldwide is the direct oxidation of ethylene. In Western Europe there is also some capacity for the production of acetaldehyde by oxidation of ethanol (<15%) and hydration of acetylene (2%). In Eastern Europe the hydration of acetylene is even more important. Only the manufacturing by means of direct oxidation of ethylene (Wacker process) is described here.

Nevertheless, ethylene is now the most important starting material for the production of acetaldehyde and most of the present capacity works by its direct oxidation (Wacker process). One- and two-stage versions of the process are on stream. In the *one-stage method*, an ethylene-oxygen mixture reacts with the catalyst solution. In the *two-stage process* the reaction is carried out with ethylene and then with oxygen in two separate reactors. The catalyst solution is alternately reduced and oxidized. At the same time the degree of oxidation of the catalyst changes alternately. Air is used instead of pure oxygen for the catalyst oxidation.

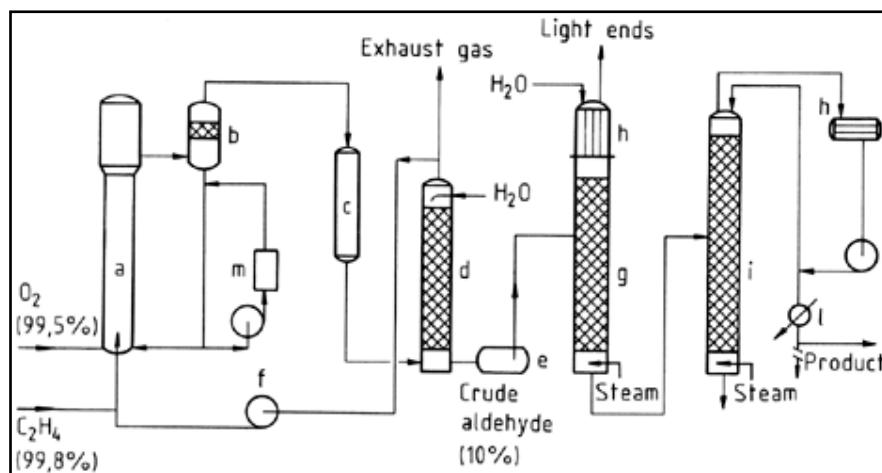
One-Stage Process

Fig. 1.1 shows the one-stage process. Ethylene and oxygen are charged into the lower part of the reaction tower (a); the catalyst is circulated via the separating vessel (b) by the airlift principle and thor-

oughly mixed with the gas. Reaction conditions are about 130 °C and 400 kPa. An acetaldehyde – water vapor mixture, together with unreacted gas, is withdrawn from the separating vessel; from this mixture the reaction products are separated by cooling (c) and washing with water (d); unreacted gas is returned to the reactor. A small portion is discharged from the cycle gas as exhaust gas to prevent accumulation of inert gases in the cycle gas; these inert gases are either introduced as contamination of the feed gas (nitrogen, inert hydrocarbons) or formed as byproducts (carbon dioxide). A partial stream of catalyst is heated to 160 °C (m) to decompose byproducts that have accumulated in the catalyst.

Crude acetaldehyde obtained during washing of the reaction products is distilled in two stages. The first stage (g) is an extractive distillation with water in which lights ends having lower boiling points than acetaldehyde (chloromethane, chloroethane, and carbon dioxide) are separated at the top, while water and higher-boiling byproducts, such as acetic acid, crotonaldehyde, or chlorinated acetaldehydes, are withdrawn together with acetaldehyde at the bottom. In the second column (i) acetaldehyde is purified by fractional distillation.

Fig. 1.1 Production of acetaldehyde by means of the direct oxidation of ethylene. One-stage process. (Taken from Fleischmann (2000): Fig. 2)



a) Reactor; b) Separating vessel; c) Cooler; d) Scrubber; e) Crude aldehyde tank; f) Cycle-gas compressor; g) Light-ends distillation; h) Condensers; i) Purification column; l) Product cooler; m) Regeneration

Two-Stage Process

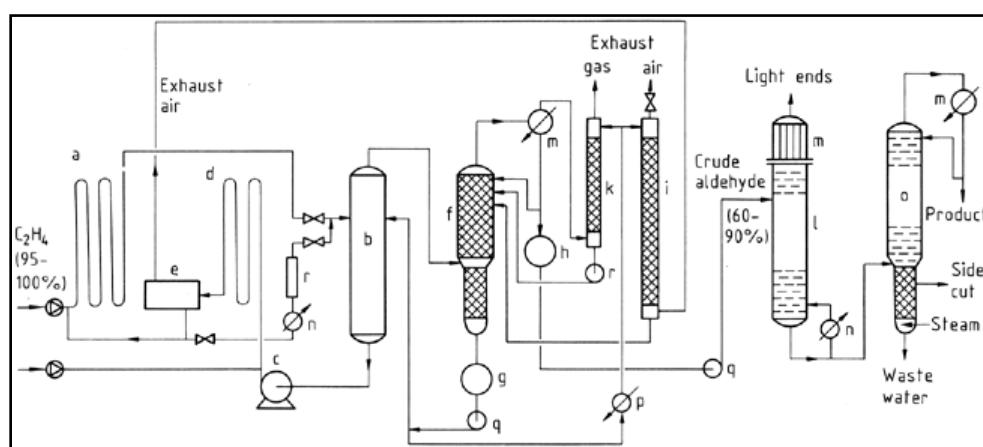
Fig. 1.2 shows the two-stage process. Tubular reactors (a), (d) are used for both “reaction” and “oxidation”. The gases react almost completely in the presence of the catalyst. Reaction of ethylene takes place at 105 – 110 °C and 900 – 1000 kPa. Catalyst solution containing acetaldehyde is then expanded in a flash tower (b) by reducing the pressure to atmospheric level. An acetaldehyde – water vapor mixture distills overhead while catalyst is sent via the pump (c) to the oxidation reactor (d), in which it reacts with oxygen at about 1000 kPa. As oxidation and reaction are carried out separately, no high-purity starting gas is required. Generally, air is used instead of oxygen. Oxygen conversion is almost complete; the exhaust air from (e) can be used as inert gas for plant use. The oxidized catalyst solution separated from exhaust air in the separator (e) is reused for the reaction with ethylene in (a).

Acetaldehyde – water vapor mixture from the flash tower (b) is preconcentrated in column (f) to 60 – 90 % acetaldehyde by utilizing the heat of reaction. Process water discharged at the bottom of (f) is returned to the flash tower to maintain a constant catalyst concentration. A portion of the process water is used for scrubbing exhaust air (nitrogen from the “oxidation”) in (i) and exhaust gas (inert gas from the “reaction”) in (k) free of acetaldehyde. Scrubbe rwater then flows to the crude aldehyde column (f).

A two-stage distillation of the crude acetaldehyde follows. In the first stage (l), low-boiling substances, such as chloromethane, chloroethane and carbon dioxide, are separated. In the second stage (o), water and higher-boiling byproducts, such as chlorinated acetaldehydes and acetic acid, are removed from acetaldehyde, and the latter is obtained in pure form overhead. Chlorinated acetaldehydes become concentrated within the column as medium-boiling substances and are discharged laterally. From this mixture, monochloroacetaldehyde can be obtained as the hemihydrate. Residual byproducts can be returned to the catalyst for oxidative decomposition. This oxidative self-purification is supported by thermal treatment of a partial stream of catalyst at about 160 – 165 °C (regeneration, r).

When gas mixtures obtained in naphtha cracking processes are used as raw material, conventional towers are used as reactors instead of coiled pipes. So far, these processes have not been developed industrially.

Fig. 1.2 Production of acetaldehyde by means of the direct oxidation of ethylene. Two-stage process. (Taken from Fleischmann (2000): Fig. 3)



a) Reactor; b) Flash tower; c) Catalyst pump; d) Oxidation reactor; e) Exhaust-air separator; f) Crude-aldehyde column; g) Process-water tank; h) Crude-aldehyde container; i) Exhaust-air scrubber; k) Exhaust-gas scrubber; l) Light-ends distillation; m) Condensors; n) Heater; o) Purification column; p) Cooler; q) Pumps; r) Regeneration

Comparison of the two methods.

In both one- and two-stage processes the acetaldehyde yield is about 95 % and the production costs are virtually the same. The advantage of using dilute gases in the two-stage method is balanced by higher investment costs. Generally, the choice of method is governed by the raw material and energy situations as well as by the availability of oxygen at a reasonable price.

Generation of by-products

The manufacturing of acetaldehyde by direction oxidation of ethylene (one- or two-stage process) generates also chlorinated hydrocarbons, chlorinated acetaldehydes, and acetic acid as byproducts.

1.3.2 Use

Acetaldehyde is used in the manufacturing of acetic acid, acetic anhydride, acetate esters, pyrine and pyridine bases, peracetic acid, 1,3-butylene glycol, and others. In 1993 acetic acid production represented 40% of the worldwide acetaldehyde demand.

1.4 System characterisation

This report corresponds to the module in the ecoinvent database for the **production of 1 kg acetaldehyde, at plant, in Europe**. For this study the production of acetaldehyde by means of the **direct oxidation of ethylene** (Wacker process) is considered. **All data in the present report are referred to 1 kg acetaldehyde 100%**.

The system includes the process with consumption of raw materials, energy, infrastructure and land use as well as the generation of solid wastes and emissions to air and water. It also includes transportation of the raw materials and wastes. Because of the lack of data on auxiliaries, no values can be presented and therefore, the transportation and consumption of auxiliaries are not included.

By-products generated in the manufacturing process are not considered. For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage and transportation of the final product are also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers.

It is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

1.5 Acetaldehyde production process

1.5.1 Data sources

The source used is von Däniken *et al.* (1995), a survey from the Swiss Agency for the Environment, Forests and Landscape (BUWAL). For acetaldehyde, the authors base on literature data for the production of ethylene oxide, since they consider that the processes are similar enough. Their literature sources are Manders (1992)¹, Pittenger *et al.* (1993)² and Wells (1991)³.

1.5.2 Raw materials and auxiliaries

von Däniken *et al.* (1995) indicates a consumption of 6.70 E-01 kg ethylene per kg acetaldehyde produced. There is no further information available about the amounts of auxiliaries used in the manufacturing process.

1.5.3 Energy and transportation

Energy

von Däniken *et al.* (1995) presents values for consumption of electricity and steam. Based on the latter (1.20 MJ per kg acetaldehyde), they calculate the consumption of different energy carriers. The information regarding consumption of energy as presented in the mentioned source, is shown in Tab. 1.2.

¹ Manders (1992): Manders E. (1992) Milieumatenstudie voor vier Bouwverven. Technische Universität Eindhoven, Fakultät Baukunde, Novem (Hrsg, Nederlandse maatschappij voor energie en milieu bv)

² Pittenger *et al.* (1993): Pittenger C. A. *et al.* (1993) Environmental Life-Cycle Inventory of Detergent-Grade Surfactant Sourcing and Production. JAOCS, Vol. 70, january.

³ Wells (1991): Wells G. M. (1991) Handbook of Petrochemicals and Processes, Gower Verlag.

Tab. 1.2 Energy consumption for the production of acetaldehyde by means of direct oxidation of ethylene (Taken from von Däniken et al. 1995)

Input		Value (kg ⁻¹ acetaldehyde)
electricity	kWh	5.00 E-02
hardcoal	MJ	1.18 E+00
heavy fuel oil	MJ	6.92 E-01
light fuel oil	MJ	1.55 E-01
natural gas	MJ	1.76 E+00

Transportation

No information is available in the source consulted concerning transportation of raw materials, auxiliaries or solid wastes. Therefore, for raw materials the following standard distances as defined in Frischknecht *et al.* (2007) are used: 100 km by lorry 32t and 600 km by train. For the transportation of the different wastes produced within the process it is assumed that they are sent to landfill and, again, standard distances are used: 10 km by lorry to disposal site. Additionally, it is assumed that this lorry has a capacity of 32 tonnes in order to facilitate the calculations. No estimation of transport amounts can be made for auxiliaries because there are no values even for consumption. Tab. 1.3 summarises the total transport amounts for the production of 1 kg acetaldehyde.

Tab. 1.3 Total transport amounts for the production of acetaldehyde by means of direct oxidation of ethylene.

(tkm. kg ⁻¹ acetaldehyde)	lorry	train
raw material	6.70 E-02	4.02 E-02
auxiliaries	nd	nd
waste to disposal sites	1.21 E-04	0
Total transports	6.71 E-02	4.02 E-01

nd: no data available

1.5.4 Infrastructure and land use

There is no information available about infrastructure and land-use of acetaldehyde plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. For this study, the estimated value is 4.00 E-10 unit. kg⁻¹ chemical.

1.5.5 Emissions to air and water

von Däniken *et al.* (1995) presents values for specific process emissions. Emissions arised by the use of the different energy carriers are included in the correspondig modules and therefore are not further discussed here. Tab. 1.4 shows the information concerning process emissions into air and into water, as presented in the mentioned source.

Tab. 1.4 Process emissions to air and water from the production process of acetaldehyde by means of direct oxidation of ethylene (Taken from von Däniken *et al.* 1995)

Process emissions ¹	Value (kg ⁻¹ acetaldehyde)	
Emissions to air		
Hydrocarbons	kg	1.09 E-02
Dust	kg	3.00 E-06
SO ₂	kg	1.00 E-06
NOx	kg	2.40 E-04
CO	kg	4.00 E-05
Emissions to water		
BOD	kg	1.60 E-03
COD	kg	2.70 E-03
Suspended solids	kg	1.40 E-05
Dissolved solids	kg	1.10 E-04
Hydrocarbons	kg	5.00 E-05
Chrome III	kg	0.02 E-05

¹: Emissions corresponding to the use of energy carriers are not included.

Dust is reported as Particulates and the value is splitted in the three fractions in use in ecoinvent database: Particulates, < 2.5 um; Particulates, > 2.5 um and < 10 um and Particulates, > 10 um. It is assumed that each fraction contributes with 33.3% to the total. Emission to air of unspecified hydrocarbons is reported as "Hydrocarbons, aliphatic, alkanes, unspecified" since this is most approximated module available in ecoinvent database.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. Basing on this assumption and doing the necessary conversion from kWh to MJ is done according to Frischknecht *et al.* (2007). Thus, considering the energy input of 5.00 E-02 kWh. kg⁻¹ acetaldehyde, the value of waste-heat taken for this study is 1.80 E-01 MJ.kg⁻¹ acetaldehyde.

1.5.6 Wastes

von Däniken *et al.* 1995 mentions the generation of 1.21 E-02 kg solid waste per kg acetaldehyde manufactured. For this study, solid waste is reported as "disposal, municipal solid waste, 22.9 %water, to sanitary landfill", due to lack of further information about the composition of the wastes mentioned. This is considered the most appropriate among the different modules available in the database.

1.6 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. The values are an estimation based on values corresponding to the manufacture of another chemical. This leads to high uncertainty scores.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht *et al.* (2007) (transport) resp. the very general module of an organic chemical plant are used.

Tab. 1.5 summarises the input and output data as well as the uncertainties used for the production of acetaldehyde. The values are given for the production of 1 kg of 100% acetaldehyde. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 1.9.

Tab. 1.5 Input- / Output-data for the production of acetaldehyde (expressed per kg acetadehyde produced)

Explanation	Name	Location	Unit	acetaldehyde, at plant		Uncertainty Type	StandardDeviation95%	GeneralComment			
				RER 0 kg							
				Infrastructure	Process						
Input from Technosphere	ethylene, average, at plant	RER	kg	6.70E-1	1	1.34	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	5.00E-2	1	1.34	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	hard coal, burned in industrial furnace 1-10MW	RER	MJ	1.18E+0	1	1.34	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	6.92E-1	1	1.34	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	heat, light fuel oil, at industrial furnace 1MW	RER	MJ	1.55E-1	1	1.34	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	natural gas, burned in industrial furnace >100kW	RER	MJ	1.76E+0	1	1.34	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	transport, lorry 32t	RER	km	6.71E-2	1	2.05	(4,na,na,na,na); standard distances				
	transport, freight, rail	RER	km	4.02E-1	1	2.05	(4,na,na,na,na); standard distances				
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); estimation				
	disposal, municipal solid waste, 22.9% water, to sanitary landfill	CH	kg	1.21E-2	1	1.34	(3.5,3,3,1,5); estimation				
Output air emission	acetaldehyde, at plant	RER	kg	1.00E+0							
	Heat, waste		MJ	1.80E-1	1	1.34	(3.5,3,3,1,5); calculated from electricity input				
	Hydrocarbons, aliphatic, alkanes, unspecified		kg	1.09E-2	1	2.12	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Particulates, < 2.5 um		kg	1.00E-6	1	3.12	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Particulates, > 2.5 um, and < 10um		kg	1.00E-6	1	2.12	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Particulates, > 10 um		kg	1.00E-6	1	1.65	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Sulfur dioxide		kg	1.00E-6	1	1.34	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Nitrogen oxides		kg	2.40E-4	1	1.34	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Carbon monoxide, fossil		kg	4.00E-5	1	2.12	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	BOD5, Biological Oxygen Demand		kg	1.60E-3	1	1.65	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
water emission	COD, Chemical Oxygen Demand		kg	2.70E-3	1	1.65	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Suspended solids, unspecified		kg	1.40E-5	1	1.65	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Solved solids		kg	1.10E-4	1	1.65	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Hydrocarbons, unspecified		kg	5.00E-5	1	1.65	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				
	Chromium, ion		kg	1.40E-5	1	5.13	(3.5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)				

1.7 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

1.8 Conclusions

An average European dataset for the production of acetaldehyde for the year 2000 is established. The dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on a report covering the European industry, based on statistics from the first half of the 1990s. The data are thus of a reasonable quality and can be used in quite a broad context.

1.9 EcoSpold Meta Information

ReferenceFunction	Name	acetaldehyde, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	LocalName	Acetaldehyd, ab Werk
ReferenceFunction	Synonyms	Ethanal
ReferenceFunction	GeneralComment	The process considered is the production of acetaldehyde by means of direct oxidation of ethylene. Manufacturing process starting with ethylene is considered, plus consumption of energy, infrastructure and land use, as well as generation of solid wastes and emissions into air and water. Transport of the raw materials and solid wastes is included. No by-product is generated in the process. Transportation and consumption of auxiliaries are not included due to the lack of data. Transport and storage of the final product are not included. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to landfill. Inventory refers to 1 kg 100% acetaldehyde. All numbers in the source used (von Däniken et al. 1995) are taken from the manufacturing of ethylene oxide, as an approximation.
ReferenceFunction	CASNumber	75-07-0
TimePeriod	StartDate	1995-12
TimePeriod	EndDate	1995-12
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	literature bases on data from the 1990s.
Geography	Text	
Technology	Text	The literature source used bases on numbers taken from the manufacture of ethylene oxide, as an approximation. It is not known how representative are these values for the European acetaldehyde industry
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	Transports based on standard distances of Ecoinvent. Infrastructure: proxy module used (chemical plant, organics)
Representativeness	UncertaintyAdjustments	none

1.10 References

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2 Acetic acid

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 Review: Heiko Kunst, Berlin

2.1 Introduction

Acetic acid, CH₃COOH, CAS 64-19-7, is a colourless, corrosive liquid. It has a pungent odour and is a dangerous vesicant. It is found in dilute solutions in many plant and animal systems. Vinegar (4–12% acetic acid solutions produced by the fermentation of wines) has been known for more than 5000 years.

The major producers of synthetic acid are currently the United States, Western Europe, Japan, Canada, and Mexico. The total capacity in these countries is close to 4×10⁶ t/a and production is 3×10⁶ t/a. (Agulio (1997))

Tab. 2.1 Chemical and physical properties of acetic acid

Property	Value	Unit
Molecular weight	60.05	g mol ⁻¹
Specific gravity	1.042	kg m ⁻³ at 26.21 °C
Heat of combustion, lower heating value (LHV)	14.6	MJ kg ⁻¹

2.2 Use of acetic acid

Acetic acid has a broad spectrum of applications. Over 60% of the acetic acid produced goes into polymers derived from either vinyl acetate, or cellulose. Most of the poly(vinyl acetate) is used in paints and coatings, or used for making poly(vinyl alcohol) and plastics. Cellulose acetate is used to produce acetate fibres. Acetic acid and acetate esters are used extensively as solvents.

2.3 Systems characterisation

“Acetic acid at plant” represents the Monsanto technology.

M. Overcash provides flow data from a theoretically modelled process because no production data are available.

2.4 Acetic acid, at plant

2.4.1 Process

Today, most industrial production of acetic acid is by the Monsanto process, in which carbon monoxide reacts with methanol under the influence of a rhodium complex catalyst at 180 °C and pressures of 3–4 MPa. The older BASF process uses a cobalt catalyst. It operates at 250 °C and 70 MPa, is slower than the Monsanto process and the yield is lower. Recently BP has started producing acetic acid using the Cativa process, which uses a promoted iridium catalyst package instead of the rhodium complex. (Jones (2000)) The other conditions are similar to the Monsanto process. The main overall reaction for all the technologies is:



The Monsanto process with rhodium carbonyl catalyst and iodide promoters operates with methanol efficiency of 94 to 99% and carbon monoxide efficiency of 90 to 99%⁴. The methanol loss is due to side reactions with propionic acid as the main product. The carbon monoxide is lost in the reaction with water to carbon dioxide and hydrogen. Thus the following equations are used to calculate the amount of inputs needed:

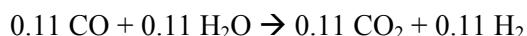
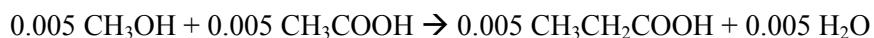
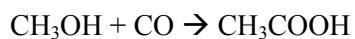


Fig. 2.1 shows the production process.

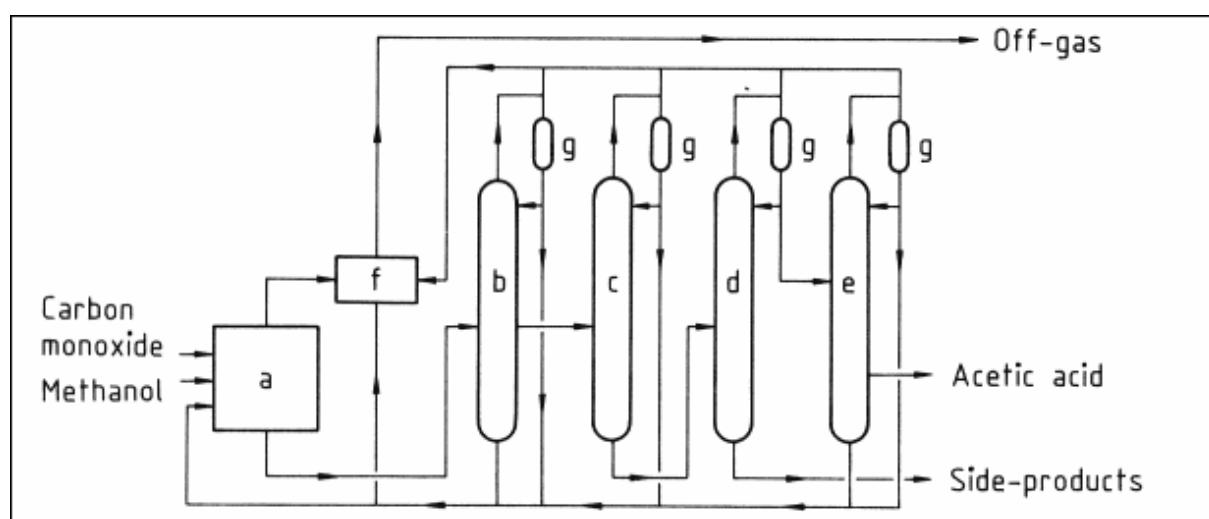


Fig. 2.1 Simplified process of acetic acid production in the Monsanto process. (Agulió (1997))

- a) Reaction system, b) Light ends column, c) Drying column, d) Heavy ends column, e) Finishing column, f) Scrubber system, g) Distillation receiver

Carbon monoxide and methanol react in (a) to produce acetic acid. The reaction and purification system vent gases are combined and scrubbed (f) to recover light ends, including organic iodides, for recycle to the reactor. Crude acetic acid is sent to a light-ends column (b). The overhead light ends and the residue are sent back to the reaction system (a), while acetic acid is removed as a side stream and sent to the drying column (c), where water is removed by conventional distillation. The overhead of the drying column, which is an acetic acid-water mixture, is sent back to the reaction system. The dry acetic acid from the base of the drying column is sent to column (d), where propionic acid is separated as a heavy end. Overhead acetic acid is sent to a finishing column (e) to produce high-purity acetic acid as a vapour side stream. Overhead and residue from the finishing towers are recycled.

Fig. 2.2 gives an overview of the in- and output flows and

Tab. 2.2 shows the ecoinvent meta data of the process.

⁴ 94.3% and 99.2% methanol and carbon monoxide efficiency from personal communication with Prof. M. Overcash, Dept. of Chemical engineering, North Carolina State University, USA, 29.10.2002

2.4.1.1 Inputs

To produce 1 kg (16.653 mol) of acetic acid 0.505 kg methanol, 0.481 kg carbon monoxide and 0.154 kg water is needed. Practically a methanol solution in water will be used instead of pure methanol and pure water.

2.4.1.2 Products

The resulting acetic acid is of 98% purity. The propionic acid (6.17 g/kg) and the hydrogen (3.66 g/kg) generated as by-products of the reaction are assumed to be used as fuel in the plant. Therefore these are not taken into account. Thus only the main product is considered relevant.

2.4.1.3 Process heat

The heat of reaction (138.6 kJ/mol) is more than high enough to provide the energy to heat the inputs to the reaction temperature. The distillation however needs additional steam (1.45MJ/kg)⁵.

2.4.1.4 Electricity

5.7E-2 kWh/kg electricity is used for compressors, fans and pumps⁵.

2.4.1.5 Catalysts

Rhodium is a platinum group element. Due to a very high price, the loss has to be minimised. The rhodium catalyst can be lost due to formation of the insoluble RhI₃ in the CO deficient areas of the plant. (Jones (2000))

Because of the presumably very low consumption of the catalyst and because no suitable LCI data are available, the use of catalyst is neglected in the LCI.

2.4.2 Emissions

2.4.2.1 Waste heat

The electricity consumed is considered as waste heat emission.

2.4.2.2 Emissions to air

The off-gas contains CO₂, CO, H₂ and VOC. It can be assumed that part of it is used as fuel or flared.

2.4.2.3 Emissions to water

The acetic acid contained in waste water is diluted, neutralised, and then degraded biologically. The waste water might be heavy metal contaminated from the catalyst. For the lack of information, no water emissions are taken account of. The amount of waste water is calculated (mass balance).

2.4.2.4 Emissions to soil

The process induces no direct soil emissions. Indirect emissions (e.g. via waste treatment) are not taken account of.

2.4.2.5 Spent catalysts

The catalyst waste is neglected because the catalyst input is neglected too.

2.4.3 Transport

The standard distances and means of transport (Frischknecht et al. 2003) are assumed for the transportation of the input materials to the production plant.

⁵ Personal communication, Ben Painter, Titanwood, 14.9.2006

2.4.4 Infrastructure

The unspecific chemical production plant is taken into account to consider the infrastructure for the process (cf. part I, Chapter 2.7).

2.5 Data quality considerations

Data are derived from theoretical knowledge of the production process. No measured data have been available.

While the masses of inputs and products are believed to be quite accurate, the energy consumption is a rough estimate.

Tab. 2.2 Meta data of acetic acid production process

Name	acetic acid, 98% in H₂O, at plant
Location	RER
Infrastructure Process	0
Unit	kg
Data Set Version	2.0
Included Processes	Production including refining.
Amount	1
Local Name	Essigsäure, 98% in H ₂ O, ab Werk
Synonyms	Ethansäure
General Comment to reference function	Theoretical data from process analysis. Only the most important flows are taken into account. Energy demand is calculated.
CAS Number	64-19-7
Start Date	1997
End Date	2000
Data Valid For Entire Period	1
Other Period Text	
Geography text	
Technology text	The process stands for the Monsanto process in which methanol reacts with carbon monoxide under the influence of a rhodium catalyst. It is assumed that 50% of the off-gas is burned as fuel, thus VOC emissions are reduced and CO ₂ is higher.
Representativeness [%]	
Production Volume	Unknown
Sampling Procedure	Theoretical model
Extrapolations	None

2. Acetic acid

General Flow information				Representation in ecoinvent							Uncertainty information					
Input	Process Name	Output	Remarks	Category	Sub category	Infrastructure	Location	Module name in ecoinvent	Mean value	Unit	Source mean value	Type	StDv 95%	General Comment		
Methanol	→			chemicals	organics	No	GLO	methanol, at plant	5.05E-01	kg	M. Overcash, personal communication	1	1.45	(4,2,4,2,3,5)		
Carbon monoxide	→			chemicals	inorganics	No	RER	carbon monoxide, CO, at plant	4.81E-01	kg	M. Overcash, personal communication	1	1.45	(4,2,4,2,3,5)		
water	→			water supply	production	No	RER	water, decarbonised, at plant	1.54E-01	kg	M. Overcash, personal communication	1	1.45	(4,2,4,2,3,5)		
rhodium compounds (catalyst)	→		not inventoried						n.A.							
methyl iodide (promotor)	→		not inventoried						n.A.							
Steam	→			chemicals	organics	No	RER	heat, unspecific, in chemical plant	1.45E+00	MJ	B. Painter, Titanwood, personal communication	1	2.56	(5,5,5,5,5,5)		
Electricity	→			electricity	production mix	No	UCTE	electricity, medium voltage, production UCTE, at grid	5.70E-02	kWh	B. Painter, Titanwood, personal communication	1	2.56	(5,5,5,5,5,5)		
Cooling water	→			resource	in water			Water, cooling, unspecified natural origin	7.80E-02	m3	B. Painter, Titanwood, personal communication	1	2.56	(5,5,5,5,5,5)		
Transport rail	→		standard distance for raw material transport	transport systems	train	No	RER	transport, freight, rail	5.92E-01	tkm	estimate	1	3.22	(5,5,5,5,5,5)		
Transport lorry	→		standard distance for raw material transport	transport systems	road	No	RER	transport, lorry >16t, fleet average	9.86E-02	tkm	estimate	1	3.22	(5,5,5,5,5,5)		
Infrastructure (plant) [unit]	→			chemicals	organics	Yes	RER	chemical plant, organics	4.00E-10	unit	estimate	1	4.25	(5,5,5,5,5,5)		
	→			Waste heat	air	unspecified		Heat, waste	2.05E-01	MJ	calculated	1	2.56	(5,5,5,5,5,5)		
	→			Acetic acid	air	unspecified		Acetic acid	5.00E-03	kg	M. Overcash, personal communication	1	3.22	(5,5,5,5,5,5)		
	→			Hydrogen	air	unspecified		Hydrogen	2.96E-04	kg	M. Overcash, personal communication	1	3.22	(5,5,5,5,5,5)		
	→			Methanol to air	air	unspecified		Methanol	2.53E-03	kg	M. Overcash, personal communication	1	3.22	(5,5,5,5,5,5)		
	→			Methane to air	air	unspecified		Methane, fossil	4.99E-03	kg	M. Overcash, personal communication	1	3.22	(5,5,5,5,5,5)		
	→			Carbon monoxide to air	air	unspecified		Carbon monoxide, fossil	6.32E-03	kg	M. Overcash, personal communication	1	2.79	(5,5,5,5,5,5)		
	→			Carbon dioxide	air	unspecified		Carbon dioxide, fossil	3.71E-02	kg	M. Overcash, personal communication	1	2.56	(5,5,5,5,5,5)		
	→			Waste water	calculated from mass balance	waste management	wastewater treatment	No	CH	treatment, sewage, unpolluted, to wastewater treatment, class 3	6.14E-05	m3	calculated	1	2.56	(5,5,5,5,5,5)
	→			Propionic acid (byproduct)	used as fuel --> not inventoried				6.17E-03	kg	calculated	1	2.79	(5,5,5,5,5,5)		
	→			Hydrogen (byproduct)	used as fuel --> not inventoried				3.37E-03	kg	calculated	1	2.79	(5,5,5,5,5,5)		
	→			Acetic acid, at plant		chemicals	organics	No	RER	acetic acid, 98% in H2O, at plant	1.00E+00	kg				

Fig. 2.2 In- and Output flows of the acetic acid production process

2.6 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

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3 Acetone

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Roland Hischier, Empa, St. Gallen (Changes 2007)
Review: Heiko Kunst, TU Berlin
Last Changes: 2007

3.1 Introduction

This chapter describes the production of acetone. This chemical is used primarily for the production of methylmethacrylate and methyl acrylate (polymers for reins, glazing panels etc.).

Synonyms for acetone: 2-propanone, dimethyl ketone

3.2 Reserves and resources of acetone

Acetone is an organic chemical compound. It is produced primarily from cumene by oxidation.

3.3 Characterisation of acetone

Acetone, C₃H₆O, is a colorless volatile liquid with a sweetish odor. Its molecular weight is 58.08 g/mol. Acetone melts at -94.7 °C, and boils just above 56°C. It is soluble in water, ethyl alcohol and ether. Acetone is flammable and its vapor may cause flash fires when ignited. Acetone will react strongly with oxidizing agents (Wells (1999)).

3.4 Production and use of acetone

Worldwide production of acetone in 2001 was 4.1 million tonnes, valued at about \$2 billion, according to www.manufacturing.net. According to the same source, world consumption of acetone in 2001 was 3.8 million tonnes, reports SRI. The U.S. and Western Europe accounted for around 60% of this amount; Japan and other Asian countries accounted for 27%. The global average annual growth rate in acetone consumption between 2001 and 2006 is estimated to be ca. 4 %.

According to Wells (1999), just over a quarter of acetone consumption is used for methyl methacrylate and methyl acrylate. Roughly another quarter is used for surface coatings and in the manufacture of cellulose acetate fiber. The third most important use is for the production of chemical solvents such as methyl isobutyl ketone, diacetone alcohol and others. A growing outlet is for the production of Bisphenol A.

Major plants are located in Germany, the Netherlands, Italy, the US, South Africa, Japan and Taiwan. Major producers include Shell Chemical, Enichem and Sasol, among others.

3.5 System characterization

Acetone and phenol are co-products and their production and demand are intertwined. Both chemicals are produced primarily via the oxidation of cumene, according to Wells (1999). Cumene, also known as isopropyl benzene, is produced from benzene and propylene.

3.5.1 Production of cumene (Wells, 1999)

Propylene and benzene are mixed and reacted using a catalyst. Reaction temperature is kept at 200 – 250 °C, with a pressure range of 15-35 bar. A high benzene concentration suppresses side reactions.

The reactor gases are used to heat incoming feed. Cumene is distilled; heavy bottoms contain di- and triisopropylbenzene,



Cumene has basically only one outlet, the manufacture of acetone and phenol.

1.5.2 Production of acetone by oxidation of cumene (Wells (1999))

Cumene is oxidised to cumene hydroperoxide (2) which is split to form phenol and acetone (3), using sulphuric acid. The reaction mixture is cooled and residual acid is neutralized. Acetone, together with some alpha-methylstyrene and cumene is recovered, the acetone is then purified by distillation.



Wells (1999) indicates that 2300 kg of cumene are required to produce 1000 kg of acetone with a yield of 90%. The production of the co-product phenol is not included in this figure.

3.5.2 Production of acetone by dehydrogenation of isopropyl alcohol (Wells (1999))

Another major production route for acetone, is by dehydrogenation of isopropyl alcohol. Isopropyl alcohol or isopropanol, can be produced by two production routes, both of which entail the hydration of propylene.



The isopropyl is heated until it is in the vapour phase and then reacted via catalyst. The reaction takes place at 300–450°C and at 2–3 bar. The exit gases containing isopropyl alcohol, acetone and hydrogen are cooled. Acetone is obtained by distillation.



The yield is reported to be 90 – 95% (Wells (1999))

3.6 Life cycle Inventory for acetone

The production process for acetone was assessed with data from PlasticsEurope (Boustead (2005-07)), which assumes that acetone stems from the oxidation of cumene, i.e. the isopropyl alcohol production route is not included in this inventory. The data stem from 1992 to 2001 and account for three production sites in Europe. Due to the fact that this dataset is cumulated it was not possible to use the other processes modelled in ecoinvent to obtain a transparent process chain. The data was nevertheless used because it represents a high share of the European production of this type of chemicals. The transformation for the data as given in Boustead (2005-07) to the data format in ecoinvent is described in detail in the methodology part of the plastics part in Hischier (2007).

Within the module assessed here there are only the resources and emissions considered which are given in the data source. Therefore no land use could be included and no direct soil emissions within

the process chain are stated. For each waste type used in the original dataset, an appropriate waste process from the ecoinvent modules was included.

3.7 Data quality considerations

Tab. 3.1 to Tab. 3.3 summarize the resulting data of the acetone production in Europe. According to the methodological remarks in Hischier (2007), these data contain no uncertainty information. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 3.12.

Tab. 3.1 Input data and functional unit outflow of the dataset for acetone production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	acetone, liquid, at plant	uncertaintyType	standardDeviation95%	GeneralComment
	662	Location		RER			
	493	InfrastructureProcess		0			
	403	Unit	kg				
Resources	Oil, crude, in ground	kg	5.88E-01				Uncertainty for LCI results cannot be determined
	Gas, natural, in ground	Nm3	9.43E-01				Uncertainty for LCI results cannot be determined
	Coal, hard, unspecified, in ground	kg	9.25E-02				Uncertainty for LCI results cannot be determined
	Coal, brown, in ground	kg	3.27E-06				Uncertainty for LCI results cannot be determined
	Peat, in ground	kg	1.94E-04				Uncertainty for LCI results cannot be determined
	Wood, unspecified, standing	m3	6.98E-07				Uncertainty for LCI results cannot be determined
	Energy, potential (in hydropower reservoir), converted	MJ	1.38E-01				Uncertainty for LCI results cannot be determined
	Uranium, in ground	kg	4.03E-06				Uncertainty for LCI results cannot be determined
	Energy, gross calorific value, in biomass	MJ	1.13E-01				Uncertainty for LCI results cannot be determined
	Barite, 15% in crude ore, in ground	kg	2.31E-06				Uncertainty for LCI results cannot be determined
	Aluminium, 24% in bauxite, 11% in crude ore, in ground	kg	1.92E-06				Uncertainty for LCI results cannot be determined
	Clay, bentonite, in ground	kg	1.38E-04				Uncertainty for LCI results cannot be determined
	Anhydrite, in ground	kg	1.38E-05				Uncertainty for LCI results cannot be determined
	Calcite, in ground	kg	3.59E-03				Uncertainty for LCI results cannot be determined
	Clay, unspecified, in ground	kg	1.38E-09				Uncertainty for LCI results cannot be determined
	Chromium, 25.5% in chromite, 11.6% in crude ore, in ground	kg	1.30E-10				Uncertainty for LCI results cannot be determined
	Copper, 0.99% in sulfide, Cu 0.36% and Mo 8.2E-3% in crude ore, in ground	kg	1.04E-06				Uncertainty for LCI results cannot be determined
	Dolomite, in ground	kg	6.08E-06				Uncertainty for LCI results cannot be determined
	Iron, 46% in ore, 25% in crude ore, in ground	kg	4.97E-04				Uncertainty for LCI results cannot be determined
	Feldspar, in ground	kg	9.61E-17				Uncertainty for LCI results cannot be determined
	Manganese, 35.7% in sedimentary deposit, 14.2% in crude ore, in ground	kg	6.41E-07				Uncertainty for LCI results cannot be determined
	Fluorspar, 92%, in ground	kg	2.91E-07				Uncertainty for LCI results cannot be determined
	Granite, in ground	kg	6.26E-15				Uncertainty for LCI results cannot be determined
	Gravel, in ground	kg	1.83E-06				Uncertainty for LCI results cannot be determined
	Cinnabar, in ground	kg	1.41E-07				Uncertainty for LCI results cannot be determined
	Magnesite, 60% in crude ore, in ground	kg	2.43E-16				Uncertainty for LCI results cannot be determined
	Nickel, 1.98% in silicates, 1.04% in crude ore, in ground	kg	2.14E-11				Uncertainty for LCI results cannot be determined
	Olivine, in ground	kg	4.67E-06				Uncertainty for LCI results cannot be determined
	Lead, 5.0% in sulfide, Pb 3.0%, Zn, Ag, Cd, In, in ground	kg	3.97E-07				Uncertainty for LCI results cannot be determined
	Phosphorus, 18% in apatite, 12% in crude ore, in ground	kg	1.34E-04				Uncertainty for LCI results cannot be determined
	Sylvite, 25 % in sylvinite, in ground	kg	1.74E-07				Uncertainty for LCI results cannot be determined
	TiO2, 95% in rutile, 0.40% in crude ore, in ground	kg	5.07E-33				Uncertainty for LCI results cannot be determined
	Sulfur, in ground	kg	2.39E-03				Uncertainty for LCI results cannot be determined
	Sand, unspecified, in ground	kg	4.96E-04				Uncertainty for LCI results cannot be determined
	Shale, in ground	kg	3.91E-05				Uncertainty for LCI results cannot be determined
	Sodium chloride, in ground	kg	7.55E-02				Uncertainty for LCI results cannot be determined
	sodium nitrate, in ground	kg	7.29E-16				Uncertainty for LCI results cannot be determined
	Talc, in ground	kg	2.20E-27				Uncertainty for LCI results cannot be determined
	Zinc, 9.0% in sulfide, Zn 5.3%, Pb, Ag, Cd, In, in ground	kg	1.57E-08				Uncertainty for LCI results cannot be determined
Input from Technosphere	Water, unspecified natural origin	m3	3.10E-03				Uncertainty for LCI results cannot be determined
	Water, river	m3	1.04E-04				Uncertainty for LCI results cannot be determined
	Water, salt, ocean	m3	3.31E-04				Uncertainty for LCI results cannot be determined
	Water, well, in ground	m3	1.96E-10				Uncertainty for LCI results cannot be determined
	Water, cooling, unspecified natural origin	m3	7.87E-02				Uncertainty for LCI results cannot be determined
	disposal facilities, chemical production	kg	1.42E-05				Uncertainty for LCI results cannot be determined
	disposal, hard coal mining waste tailings, in surface backfill	kg	1.95E-02				Uncertainty for LCI results cannot be determined
	disposal, municipal solid waste, 22.9% water, to municipal incineration	kg	2.59E-03				Uncertainty for LCI results cannot be determined
	disposal, average incineration residue, 0% water, to residual material landfill	kg	7.32E-03				Uncertainty for LCI results cannot be determined
	disposal, wood untreated, 20% water, to municipal incineration	kg	9.18E-06				Uncertainty for LCI results cannot be determined
	disposal, plastics, mixture, 15.3% water, to municipal incineration	kg	8.22E-05				Uncertainty for LCI results cannot be determined
Output	disposal, hazardous waste, 0% water, to underground deposit	kg	4.23E-03				Uncertainty for LCI results cannot be determined
	acetone, liquid, at plant	kg	1.00E+00				

Tab. 3.2 Emission to air data for acetone production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	acetone, liquid, at plant	uncertaintyType	standardDeviation95%	GeneralComment
Air emission	662	Heat, waste	MJ	2.90E+01	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
	493	Particulates, > 10 um	kg	1.88E-04			
	403	Particulates, > 2.5 um, and < 10um	kg	2.52E-04			
		Particulates, < 2.5 um	kg	1.47E-04			
		Carbon monoxide, fossil	kg	1.87E-03			
		Carbon monoxide, biogenic	kg	2.88E-06			
		Carbon dioxide, fossil	kg	1.79E+00			
		Carbon dioxide, biogenic	kg	2.75E-03			
		Sulfur dioxide	kg	6.87E-03			
		Hydrogen sulfide	kg	1.67E-08			
		Nitrogen oxides	kg	4.59E-03			
		Ammonia	kg	9.71E-09			
		Chlorine	kg	2.00E-08			
		Hydrogen chloride	kg	4.97E-05			
		Fluorine	kg	1.36E-10			
		Hydrogen fluoride	kg	1.87E-06			
		NMVOC, non-methane volatile organic compounds, unspecified origin	kg	3.52E-03	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
		Aldehydes, unspecified	kg	8.35E-05			
		Lead	kg	1.86E-09			
		Mercury	kg	1.35E-08			
		Sulfate	kg	1.49E-12			
		Dinitrogen monoxide	kg	7.14E-09			
		Hydrogen	kg	6.38E-05			
		Ethane, 1,2-dichloro-	kg	1.09E-10			
		Ethene, chloro-	kg	4.00E-10			
		Halogenated hydrocarbons, chlorinated	kg	4.29E-09			
		Cyanide	kg	7.64E-19			
		Methane, fossil	kg	1.71E-02	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
		Methane, biogenic	kg	2.63E-05			
		Hydrocarbons, aromatic	kg	2.66E-05	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
		Hydrocarbons, aliphatic, alkanes, cyclic	kg	1.62E-06			
		Carbon disulfide	kg	4.65E-11			
		Methane, dichloro-, HCC-30	kg	5.64E-11	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
		Copper	kg	1.71E-09			
		Arsenic	kg	8.14E-11			
		Cadmium	kg	2.04E-11	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
		Silver	kg	5.63E-12			
		Zinc	kg	2.56E-10			
		Chromium	kg	8.90E-07	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
		Selenium	kg	1.95E-13			
		Nickel	kg	1.62E-06			
		Antimony	kg	3.88E-14	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
		Ethene	kg	2.26E-06			
		Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin	kg	5.28E-32			
		Benzene	kg	5.40E-06	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
		Toluene	kg	9.15E-07			
		Xylene	kg	3.78E-07			
		Benzene, ethyl-	kg	3.05E-07	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined	Uncertainty for LCI results cannot be determined
		Styrene	kg	5.40E-08			
		Propene	kg	1.67E-06			

Tab. 3.3 Emission to water data for acetone production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	acetone, liquid, at plant	RER o kg	uncertaintyType	standardDeviation95%	GeneralComment
	662	Location						
	493	Infrastructure						
	403	Process						
Water emission	COD, Chemical Oxygen Demand		kg	4.35E-04				Uncertainty for LCI results cannot be determined
	BOD ₅ , Biological Oxygen Demand		kg	2.04E-05				Uncertainty for LCI results cannot be determined
	Lead		kg	3.64E-10				Uncertainty for LCI results cannot be determined
	Iron, ion		kg	3.88E-08				Uncertainty for LCI results cannot be determined
	Sodium, ion		kg	7.12E-03				Uncertainty for LCI results cannot be determined
	Acidity, unspecified		kg	1.05E-06				Uncertainty for LCI results cannot be determined
	Nitrate		kg	2.67E-06				Uncertainty for LCI results cannot be determined
	Mercury		kg	3.71E-09				Uncertainty for LCI results cannot be determined
	Ammonium, ion		kg	1.93E-06				Uncertainty for LCI results cannot be determined
	Chloride		kg	2.55E-03				Uncertainty for LCI results cannot be determined
	Cyanide		kg	4.71E-11				Uncertainty for LCI results cannot be determined
	Fluoride		kg	4.88E-09				Uncertainty for LCI results cannot be determined
	Sulfide		kg	1.01E-09				Uncertainty for LCI results cannot be determined
	Hydrocarbons, unspecified		kg	7.67E-04				Uncertainty for LCI results cannot be determined
	Suspended solids, unspecified		kg	6.23E-04				Uncertainty for LCI results cannot be determined
	Oils, unspecified		kg	1.12E-05				Uncertainty for LCI results cannot be determined
	Chlorinated solvents, unspecified		kg	1.24E-06				Uncertainty for LCI results cannot be determined
	Chlorine		kg	1.19E-09				Uncertainty for LCI results cannot be determined
	Phenol		kg	5.66E-07				Uncertainty for LCI results cannot be determined
	Solved solids		kg	1.18E-03				Uncertainty for LCI results cannot be determined
	Phosphorus		kg	1.34E-04				Uncertainty for LCI results cannot be determined
	Nitrogen		kg	4.14E-06				Uncertainty for LCI results cannot be determined
	Sulfate		kg	7.24E-03				Uncertainty for LCI results cannot be determined
	Ethane, 1,2-dichloro-		kg	1.81E-12				Uncertainty for LCI results cannot be determined
	Ethene, chloro-		kg	7.61E-12				Uncertainty for LCI results cannot be determined
	Potassium, ion		kg	5.24E-09				Uncertainty for LCI results cannot be determined
	Calcium, ion		kg	7.51E-06				Uncertainty for LCI results cannot be determined
	Magnesium		kg	4.10E-09				Uncertainty for LCI results cannot be determined
	Chromium, ion		kg	9.91E-13				Uncertainty for LCI results cannot be determined
	Chlorate		kg	2.02E-05				Uncertainty for LCI results cannot be determined
	Bromate		kg	4.84E-10				Uncertainty for LCI results cannot be determined
	TOC, Total Organic Carbon		kg	4.34E-05				Uncertainty for LCI results cannot be determined
	AOX, Adsorbable Organic Halogen as Cl		kg	2.90E-12				Uncertainty for LCI results cannot be determined
	Aluminum		kg	4.12E-07				Uncertainty for LCI results cannot be determined
	Zinc, ion		kg	1.52E-08				Uncertainty for LCI results cannot be determined
	Copper, ion		kg	1.14E-07				Uncertainty for LCI results cannot be determined
	Nickel, ion		kg	8.30E-08				Uncertainty for LCI results cannot be determined
	Carbonate		kg	1.45E-04				Uncertainty for LCI results cannot be determined
	Arsenic, ion		kg	2.21E-10				Uncertainty for LCI results cannot be determined
	Cadmium, ion		kg	1.56E-13				Uncertainty for LCI results cannot be determined
	Manganese		kg	1.88E-12				Uncertainty for LCI results cannot be determined
	Tin, ion		kg	6.74E-15				Uncertainty for LCI results cannot be determined
	Strontium		kg	2.28E-09				Uncertainty for LCI results cannot be determined
	Silicon		kg	4.75E-20				Uncertainty for LCI results cannot be determined
	Benzene		kg	4.52E-19				Uncertainty for LCI results cannot be determined
	Molybdenum		kg	-				Uncertainty for LCI results cannot be determined

3.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

3.9 Conclusions

The inventory data used in this process does not give transparency on the processes used and allocations made due to the use of cumulated data. Therefore, many emissions especially soil emissions are not accounted. Because of the cumulated data also no land occupation and land transformation could be included in the dataset. This leads to an incompleteness of the dataset, which has to be considered when using it. Also the uncertainty of the data used could not be determined for those datasets. Nevertheless the data refers on a large share of the European production and should therefore be representative for the production of this chemical.

3.10 EcoSpold Meta Information

ReferenceFunction	401	Name	acetone, liquid, at plant
Geography	662	Location	RER
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	402	IncludedProcesses	Aggregated data for all processes from raw material extraction until delivery at plant
ReferenceFunction	404	Amount	1
ReferenceFunction	490	LocalName	Aceton, flüssig, ab Werk
ReferenceFunction	491	Synonyms	
ReferenceFunction	492	GeneralComment	Data are from the Eco-profiles of the European plastics industry (PlasticsEurope). Not included are the values reported for: recyclable wastes, amount of air / N ₂ / O ₂ consumed, unspecified metal emission to air and to water, mercaptan emission to air, unspecified CFC/HCFC emission to air, dioxin to water. The amount of "sulphur (bonded)" is assumed to be included into the amount of raw oil.
ReferenceFunction	502	CASNumber	67-64-1
TimePeriod	601	StartDate	1992
TimePeriod	602	EndDate	2001
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	time to which data refer
Geography	663	Text	3 European plants (NL, D)
Technology	692	Text	production by oxidation of cumene
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	worldwide 4.1 Mt in 2001
Representativeness	725	SamplingProcedure	literature values based on company survey
Representativeness	726	Extrapolations	no extrapolation
Representativeness	727	UncertaintyAdjustments	none

3.11 References

- Boustead (2005-07) Boustead I. (2005-07) Electronic documents with the datasets from the PlasticsEurope Eco-Profiles - Calculation results from March 2005. Download of December 18 from <http://www.plasticseurope.org>.
- Hischier (2007) Hischier R. (2007) Life Cycle Inventories of Packaging and Graphical Paper. Final report ecoinvent data v2.0 No. 11. Swiss Centre for Life Cycle Inventories, Empa - TSL, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.
- Wells (1999) Wells M. G. (1999) Handbook of Petrochemicals and Processes, 2nd Edition. Gower Publishing Company Ltd., Ashgate (United Kingdom)

3.12 EcoSpold Meta Information

ReferenceFunction	Name	acetone, liquid, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Aggregated data for all processes from raw material extraction until delivery at plant
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Aceton, flüssig, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	Data are from the Eco-profiles of the European plastics industry (APME). Not included are the values reported for: recyclable wastes, amount of air / N ₂ / O ₂ consumed, unspecified metal emission to air and to water, mercaptan emission to air, unspecified CFC/HCFC emission to air. The amount of "sulphur (bonded)" is assumed to be included into the amount of raw oil.
ReferenceFunction	CASNumber	67-64-1
TimePeriod	StartDate	1996
TimePeriod	EndDate	1996
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	time to which data refer
Geography	Text	3 European plants (NL, D)
Technology	Text	production by oxidation of cumene
Representativeness	Percent	
Representativeness	ProductionVolume	worldwide 4.1 Mt in 2001
Representativeness	SamplingProcedure	literature values based on company survey
Representativeness	Extrapolations	no extrapolation
Representativeness	UncertaintyAdjustments	none

4 Acetylene

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 Review: Heiko Kunst, Berlin

4.1 Introduction

Acetylene, ethyne, C_2H_2 , CAS 74-86-2 is the simplest hydrocarbon with a triple bond. The most important properties are given in Tab. 4.1.

Tab. 4.1 Chemical and physical properties of acetylene (Pässler et al. (1997), Bach et al. (1999))

Property	Value	Unit
Molecular weight	26.03	$g\ mol^{-1}$
Heating value	51.2	MJ/kg
Specific gravity	1.17	$kg\ m^{-3}$ at 0 °C and 101.3 kPa

4.2 Use of acetylene

Due to the high temperature of oxyacetylene flames, acetylene is mainly used in the processing of meals. It is e.g. used in welding, cutting, brazing, soldering, surfacing, flame spraying, heating, hardening, straightening, cleaning, pickling, rust removal, and decarbonizing.

Acetylene used to be an important starting material for many chemical processes. In recent years however, it was more and more substituted by other olefins.

4.3 Systems characterisation

Most of the acetylene in western Europe is produced by the partial oxidation of natural gas. 5.9 m³ natural gas and 5.3 kg oxygen is needed to produce 1 kg of acetylene (yield 30%). The inputs are fed to a special furnace where they react to acetylene at 1500 °C. The gas mixture is cooled after the oxidation. Some soot can be washed out by the cooling water. The rest is retained in electro filters. The cool gas contains about 8% acetylene. The other gases, mostly CO and H₂, are either used as feedstock for other processes or burned. (Frischknecht (1999))

4.4 Acetylene, at regional storehouse

4.4.1 Process

In this study we assume that natural gas is used as feedstock and as fuel. 1.315 of the 4.7 kg natural gas input is used as feedstock. Thus 3.385 kg can be used as fuel. We assume that the burning process is similar to the burning of natural gas in industrial furnaces.

Fig. 6.2 gives an overview of the in- and output flows and

Tab. 6.2 shows the meta data of the process.

4.4.1.1 Inputs

Oxygen and natural gas are the only feedstock inputs considered. The oxygen is assumed to be produced at the acetylene production site.

4.4.1.2 Products

Acetylene is only about 8% of the produced gas. The other reaction products are separated and used outside the system boundaries.

4.4.1.3 Process heat

Burning a part of the natural gas input provides the process heat. This part of the natural gas is inventoried as "natural gas, burned in industrial furnace"

4.4.1.4 Electricity

Electricity is used for compressors, fans and the electrofilter. A consumption of 0.001 MJ per kg acetylene is assumed.

4.4.2 Emissions

4.4.2.1 Waste heat

The heat of the electricity consumed is considered as waste heat emissions. The heat of reaction is already considered in the "natural gas, burned in industrial furnace" module.

4.4.2.2 Emissions to air

The gases other than acetylene are assumed either to be recovered and used or to be burned substituting natural gas. Thus the emission of these gases is not accounted for. The only direct air emission is acetylene.

4.4.2.3 Emissions to water

Water might be used for cooling. It might be polluted by soot during the process. For a lack of information, water emissions are not taken into account.

4.4.2.4 Emissions to soil

The process induces no direct soil emissions. Indirect emissions (e.g. via waste treatment) are not taken account of.

4.4.3 Transport

There are only few acetylene producers in Europe. Thus for the transports of the acetylene to the regional storage in Switzerland 600 km of rail and 50 km of lorry transports is assumed. Twice the mass of the acetylene is used in the calculation to account for the bottles in which acetylene is transported.

4.4.4 Infrastructure

The unspecific chemical production plant is taken into account to consider the infrastructure for the process (cf. part I, Chapter 2.7).

4.5 Data quality considerations

Data are derived from theoretical knowledge of the production process. No measured data have been available.

While the masses of inputs and products are believed to be quite accurate, the energy consumption is a rough estimate. No direct emissions except for acetylene are taken into account. This, of course is an underestimation.

This dataset is of poor quality and must not be used in systems where acetylene plays an important role.

Tab. 4.2 Meta data of "acetylene, at regional storehouse"

Name	acetylene, at regional storehouse
Location	CH
Infrastructure Process	0
Unit	kg
Data Set Version	2.0
Included Processes	production and transport to Switzerland
Amount	1
Local Name	Acetylen, ab Regionallager
Synonyms	Ethin//ethyne
General Comment to reference function	Theoretical data from process analysis. Only the most important flows are taken into account. Electricity demand is estimated. Not to be used for systems where acetylene plays an important role.
Start Date	1991
End Date	2003
Data Valid For Entire Period	1
Other Period Text	
Geography text	Production in western Europe
Technology text	Partial oxidation of natural gas. The flue gas is assumed to be cleaned with electrofilters.
Representativeness [%]	
Production Volume	Unknown
Sampling Procedure	Theoretical model
Extrapolations	None
Uncertainty Adjustments	None

4. Acetylene

General Flow information				Representation in ecoinvent							Uncertainty information			
Input	Process Name	Output	Remarks	Category	Sub category	Infra structure	Loca tion	Modul name in ecoinvent	Mean value	Unit	Source mean value	Type	StDv 95%	General Comment
oxygen	→ acetylene, at regional storehouse			chemicals	inorganics	No	RER	oxygen, liquid, at plant	5.30E+00 kg		Frischknecht 1999	1	1.27	(3,3,3,2,1,5,3)
natural gas (feedstock)				natural gas	production	No	RER	natural gas, at long-distance pipeline	1.68E-03 Nm3		Frischknecht 1999	1	1.27	(3,3,3,2,1,5,3)
natural gas (fuel)				natural gas	heating systems	No	RER	natural gas, burned in industrial furnace >100kW	1.60E-01 MJ		Frischknecht 1999	1	1.27	(3,3,3,2,1,5,1)
transport rail		600 km rail, 50 km lorry to regional storage. Twice the mass to account for the bottles		transport systems	train	No	RER	transport, freight, rail	1.20E+00 tkm		estimation	1	2.09	(4,5,n.A.,n.A.,n.A.,n.A.,5)
transport lorry				transport systems	road	No	CH	transport, lorry 20-28t, fleet average	1.00E-01 tkm		estimation	1	2.09	(4,5,n.A.,n.A.,n.A.,n.A.,5)
Electricity		for pumps, filters,...		electricity	production mix	No	UCTE	electricity, medium voltage, production UCTE, at grid	2.78E-04 kWh		estimation	1	2.56	(5,5,5,5,5,2)
Infrastructure (plant) [unite]				chemicals	organics	Yes	RER	chemical plant, organics	4.00E-10 unit		estimation	1	4.25	(5,5,5,5,5,9)
waste heat	from electricity use			air	unspecified			Heat, waste	1.00E-03 MJ		estimation	1	2.56	(5,5,5,5,5,13)
acetylen to air				air	unspecified			Ethyne	1.00E-02 kg		Frischknecht 1999	1	3.22	(5,5,5,5,5,23)
acetylen, at regional storage				chemicals	organics	No	CH	acetylene, at regional storehouse	1.00E+00 kg					

Fig. 4.1 In- and Output flows of "acetylene, at regional storehouse" process

4.6 Cumulative Results and Interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

4.7 References

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5 Acrylic Acid

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Review: Heiko Kunst, TU Berlin

Last Changes:

2006

5.1 Introduction

Acrylic acid ($C_3H_4O_2$, CAS-No. 79-10-7) is a colourless, slightly water soluble liquid with an acrid odour. It belongs to the carboxylic acids. The acid may be transported stabilised with inhibitors (such as hydroquinone derivatives) to prevent polymerisation. Functionally acrylic acid may be regarded as a derivative of ethylene in which one hydrogen atom has been replaced with a carboxyl group, although this is not the basis of its synthesis. The chemical and physical properties (see Tab. 5.1) of the polymers can be modified through controlled variation in the selection and balance of the monomers, the extent of cross-linking and molecular mass. This flexibility is complemented by high resistance to chemical and environmental degradation, strength, clarity, and being readily available in high purity forms (Häussinger et al. (2000)).

Synonyms for Acrylic acid: 2-Propenoic acid; Acroleic Acid; Acrylate; Ethylenecarboxylic acid; propene acid; Propenoic acid; Vinylformic Acid.

Tab. 5.1 Chemical and physical properties of acrylic acid Chemfinder (2002).

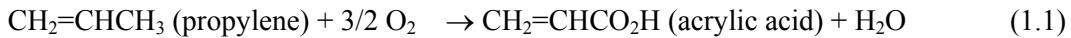
Property	Value	Unit	Property	Value	Unit
Molecular weight	72.06	$g\ mol^{-1}$	Melting point	13.5	°C
Density (at 30°C)	1.040	$G\ cm^{-3}$	Boiling point	141	°C
Water solubility	>=10	g/100 ml	Flash point	48	°C

5.2 Production Technologies and Use

5.2.1 Production process

In the past, acrylic acid was produced by a variety of different processes. Today, most of the commercial acrylic acid is manufactured by the oxidation of propylene (ACTED-Consultants (1995); Häussinger et al. (2000)). Two production processes can be distinguished:

- **Single-step propylene oxidation:** The yield in the single-step process is at best approximately 50-60%. Another drawback is the limited lifetime of the catalyst, which is a multicomponent system composed of polyvalent oxides with molybdenum oxide as main component and tellurium oxide as promotor. The disadvantages of this process lead to the development of the two-step process.



- **Two-step propylene oxidation:** The limited life of the catalyst has promoted a two stage manufacturing process via acrolein using two catalysts. The first stage is the oxidation of propylene to acrolein using a bismuth molybdate catalyst in a strongly exothermic reaction (at about 370°C). In the second stage, the acrolein gas is passed over a molybdenum vanadium oxide catalyst that is also exothermic (at about 270°C - about 100°C cooler than the first stage). The crude acrylic acid is then cooled to about 80°C, absorbed in water (30 to 60% concentration) and extracted with organic solvent or water (depending on the concentration).





In a subsequent step, acrylic acid is separated from the large volume of water present in the absorber effluent. This purification runs either by distillation from the solvent or by removing from water with added inhibitors to minimise the formation of polymers. Conversion rates of up to 90 per cent are achievable at commercial scales of production depending on technology, catalysts and conditions.

5.2.2 Production technology

A technical grade of acrylic acid may be produced by a simple distillation to produce a grade of acid suitable for the manufacture of acrylic esters, but unsuitable for polymerisation. For esters, whose manufacture is normally integrated with an acrylic acid plant, the purification step is undertaken after the esterification process. A typical process flow diagram of a single-step distillation plant is shown in Fig. 5.1.

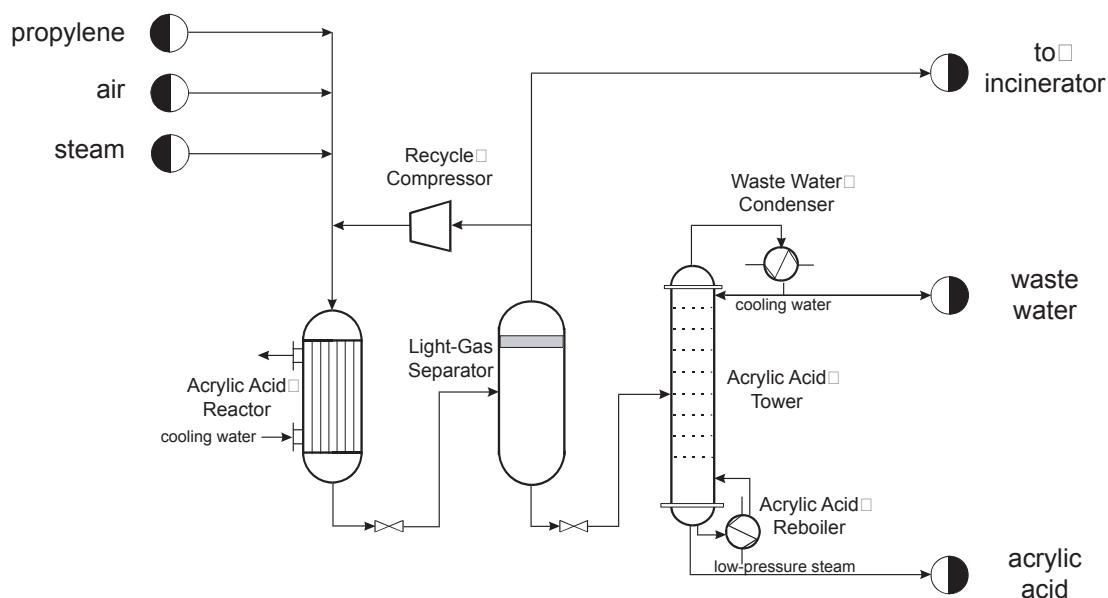


Fig. 5.1 Process flow diagram for acrylic acid production.

A high purity form (often referred to as *glacial* acrylic acid) is produced by a second distillation or crystallisation that reduces aldehyde impurities (especially furfural) which inhibit polymerisation. Different grades of glacial acrylic acid are available with flocculants requiring higher purity levels than dispersants and some other applications.

Though all based on the same principle, there are different catalysts, conditions and systems to produce acrylic acid with variation in production efficiencies and the quality of finished product. There is only limited technology available to produce acrylic acid. Most manufacturing plants use the Japanese Nippon Shokubai process (including Rohm and Haas) and another licensor is Mitsubishi Yuka. BASF however, the largest scale manufacturer of acrylic acid and esters, does not release its technology. It is worth noting that technical difficulties have been reported as for example during 1995, Idemitsu Petrochemical Company, and the Sumitomo Chemical Company failed to operate above two-thirds capacity after adding to plant capacity.

5.2.3 Use of acrylic acid

The annual world production of acrylic acid is about 2.4 million tonnes and is growing at about 4% per year (Dieterle (2001); Häussinger et al. (2000)). Acrylic acid is a versatile chemical that can be esterified, aminated or otherwise modified and polymerised to complex molecular arrangements to suit requirements. This characteristic enables a broad range of reactions for providing performance characteristics to a range of polymers. The esters are produced by reacting acrylic acid with alcohols especially ethanol, methanol and butanol that may be saponified, converted to other esters or amides by aminolysis (Häussinger et al. (2000)).

Acrylates are derivatives of acrylic acid (such as methyl and ethyl acrylate) whose properties have been sufficiently modified to enable of acrylic acid to be used in different media as emulsion and solution polymers. As emulsions, these products may be used as coatings, finishes and binders leading to applications in paints, adhesives, and polishes with solutions used for industrial coatings. Two-third of the world's production of acrylic acid is used to produce acrylic esters (acrylates) primarily for use in emulsions and solution polymers for latex-based paints, coatings, adhesives and textiles.

Polymers of acrylic acid can be produced as superabsorbent materials (e.g. for diapers), and soluble as a replacement for phosphates in detergents. Both of these represent fast growing applications for acrylic acid. The chemical and physical properties of the polymers can be modified through controlled variation in the selection and balance of the monomers, the extent of cross-linking and molecular mass. This flexibility is complemented by high resistance to chemical and environmental degradation, strength, clarity, and being readily available in high purity forms.

5.3 Systems characterization

Propylene is the only feedstock used in acryl acid plants installed since 1970 and most of commercial acrylic acid is now produced by the acrolein process using two different catalysts. Thus, the dataset of the ecoinvent project is also based on the two-step propylene oxidation. The functional unit for the inventory is 1 kg of liquid acrylic acid. As process location Europe (RER) is used.

In the production process the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of acrylic acid is not considered to be high.

5.4 Acrylic acid, at plant (RER)

5.4.1 Process

This dataset includes a rough estimation of the production process of acrylic acid by the two-step oxidation out of propylene. Main input data are taken from a Australian report (ACTED-Consultants (1995)), while the emissions to air and water were estimated using mass balance. It was assumed that wastewater is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is quite large. The overall reaction for the production of dimethyl ether can be formulated as follows:



A typical flow scheme for the industrial production of dimethyl ether is shown in Fig. 5.1 above.

5.4.2 Resources

Raw materials and Chemicals

For the production of acrylic acid out of propylene, ACTED-Consultants (1995) mentions the following inputs (assuming a yield of 90%):

- Propylene: 0.63 kg
- Ethyl acetate: 0.01 kg
- Hydroquinone: 0.002 kg
- Catalyst: 0.0003 kg

Out of the documents for a “companion project for curriculum” of the West Virginia University (Schaeiwitz & Turton (1998)) reports an input of 0.853 kg propylene. This data source contains no further indications about the input amounts of this process. As this dataset is quite a rough estimation, for the ecoinvent project the higher value is chosen.

Energy

According to ACTED-Consultants (1995), a natural gas amount of 0.23 MJ/kg acrylic acid is needed. There is no further energy consumption indicated in this data source nor in other data sources examined. But usually, electricity is needed to run the process auxiliaries and the wastewater treatment. In accordance with other chemicals in the ecoinvent project, an electricity amount of 1.2 MJ/kg is used here – based on the electricity consumption of a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)).

Water use

There was no information available on the amount of cooling water used within the plant, although there has to be a respective use. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the ethanolamines production. According to the ongoing IPPC activities of the European Commission, the cooling water demand may reach 86 kg kWh⁻¹ for an once through cooling system, which would lead to a cooling water demand of 48 kg per kg product for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m³ cooling water per kg product was used.

Schaeiwitz & Turton (1998) indicates a water consumption (only process water!) of 0.41 kg/kg acrylic acid produced. Due to a lack of more information, this value is used here.

Transport

Standard distances and means according to Frischknecht et al. (2007) are used for all input materials due to the fact that no information is available in Müller & Hübsch (2000).

5.4.3 Emissions

Waste heat

It was assumed that 100% of the electricity consumed is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

Schaeiwitz & Turton (1998) contains information about the complete gas outflow from the acrylic acid production. It is assumed here that this outflow is incinerated on-site in order to recover the energy content. Thus, the final outflow into the ambient air is CO₂, N₂ and water vapour. For this process a complete combustion of the excess propylene flow in this incineration flow is assumed. Diffuse losses of propylene across the complete production plant are in the order of 0.001 g/kg of produced acrylic acid⁶.

Emissions to water

According to the information in Schaeiwitz & Turton (1998), the waste water stream is only polluted with acetic acid and is supposed to go to a wastewater treatment plant (WWTP). Thus, for this study, the amount of wastewater is taken from the study of Schaeiwitz & Turton (1998) and is represented by the dataset “treatment, sewage, to wastewater treatment, class 2” due to a lack of more precise information.

Solid wastes

Solid wastes were neglected in this inventory. A summary of all values used in this inventory here for acrylic acid is given in Tab. 5.2.

⁶ Personal Communication from Consulting Company of Chemical Industry

Tab. 5.2 Energy demand, resource demand and emissions for the production of acrylic acid

[per kg acrylic acid]			Remark
INPUTS			
propylene	kg	8.53E-01	according to Schaeiwitz et al. 1998
ethyl acetate ¹	kg	1.00E-02	according to Australian study
hydrochinone ¹	kg	2.00E-03	dito
catalyst ²	kg	3.00E-04	dito
Water, unspecified	kg	4.10E-01	according to Schaeiwitz et al. 1998
Electricity, medium voltage	kWh	3.33E-01	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2.30E-01	according to Australian study
Water, cooling, unspecified	m3	2.40E-02	estimation
Transport, by train	tkm	5.19E-01	standard distances & means
Transport, by lorry	tkm	8.65E-02	standard distances & means
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
carbon dioxide, fossil, to air	kg	7.37E-01	Schaeiwitz et al. 1998 & incineration propylene
nitrogen, to air	kg	4.73E+00	according to Schaeiwitz et al. 1998
oxygen, to air	kg	2.66E-01	according to Schaeiwitz et al. 1998
propylene, to air	kg	1.00E-06	personal communication
acetic acid, to water	kg	2.88E-04	according to Schaeiwitz et al. 1998
waste water (amount)	kg	3.33E+00	according to Schaeiwitz et al. 1998

¹ shown as "chemicals organic, unspecified, at plant (GLO)"² shown as "chemicals inorganic, unspecified, at plant (GLO)"

5.4.4 Infrastructure

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module "chemical plant, organics" was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg dimethyl ether was included.

5.5 Data quality considerations

Tab. 5.3 shows the data quality indicators for the inventory of the acrylic acid production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the acrylic acid production has a quite a uncertainty, because only few data of the production processes were available. The highest uncertainties exist for the emissions. Due to missing data these values are based mainly on assumptions and approximations. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 5.8.

Tab. 5.3 Input / Output and uncertainty values for the process “acrylic acid, at plant (RER)”

Explanation	Name	Location	Unit	acrylic acid, at plant	RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment	
								Location	standardDeviation95%
								Infrastructure	Process
Resources	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); data based on estimation by big chemical plant		
	Water, unspecified natural origin		m3	4.10E-04	1	1.42	(3,5,2,5,3,5); data from 1 US source		
	propylene, at plant	RER	kg	8.53E-01	1	1.42	(3,5,2,5,3,5); data from 1 US source		
	chemicals organic, at plant	GLO	kg	1.20E-02	1	1.42	(3,5,2,5,3,5); data from 1 Australian source		
	chemicals inorganic, at plant	GLO	kg	3.00E-04	1	1.42	(3,5,2,5,3,5); data from 1 Australian source		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.42	(3,5,2,5,3,5); data from 1 Australian source		
	natural gas, burned in industrial furnace >100kW	RER	MJ	2.30E-01	1	1.42	(3,5,2,5,3,5); data from 1 Australian source		
	transport, freight, rail	RER	tkm	5.19E-01	1	2.09	(4,5,na,na,na,na); standard distances		
	transport, lorry <16t, fleet average	RER	tkm	8.65E-02	1	2.09	(4,5,na,na,na,na); standard distances		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation		
Output	acrylic acid, at plant	RER	kg	1					
Air emission	Heat, waste		MJ	1.20E+00	1	1.42	(3,5,2,5,3,5); calculated from input		
	Carbon dioxide, fossil		kg	7.37E-01	1	1.42	(3,5,2,5,3,5); calculated, based on data from 1 US source		
	Propene		kg	1.00E-06	1	1.7	(3,5,2,5,3,5); data from personal communication		
Water emission	Acetic acid		kg	2.88E-04	1	3.16	(3,5,2,5,3,5); data from 1 US source		

5.6 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

5.7 Conclusions

The inventory for acrylic acid is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if acrylic acid is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

5.8 EcoSpold Meta Information

ReferenceFunction	Name	acrylic acid, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, emissions to air and water from production, estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Acrylsäure, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid acrylic acid. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	79-10-7
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from propylene by two-step oxidation process with a process yield of 90%. Inventory bases on an two general reports about the theoretical production of acrylic acid.
Representativeness	Percent	
Representativeness	ProductionVolume	worldwide production 2.4 Mt (End of 90s)
Representativeness	SamplingProcedure	literature
Representativeness	Extrapolations	see technology and geography
Representativeness	UncertaintyAdjustments	none

5.9 References

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6 Adipic acid

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 Review: Heiko Kunst, Berlin

6.1 Introduction

Adipic acid, hexanedioic acid, 1,4–butanedicarboxylic acid, C₆H₁₀O₄, CAS 124-04-9, is the most significant commercially of all the aliphatic dicarboxylic acids. Appearing in nature in only minor amounts, it is synthesised on a very large scale world-wide. (Davis (1997)) Global adipic acid production is estimated to be 2.2x106 t. (Anonymous (1996))

Tab. 6.1 Chemical and physical properties of adipic acid

Property	Value	Unit
Molecular weight	146.14	g mol ⁻¹
Melting point	152.1	°C
Specific gravity	1085	kg m ⁻³ at 170 °C
Bulk density (depending on particle size)	600 – 700	kg m ⁻³

Adipic acid is isolated as colourless, odourless crystals having an acidic taste. It is very soluble in methanol and ethanol, soluble in water and acetone, and very slightly soluble in cyclohexane and benzene. Adipic acid crystallises as monoclinic prisms from water, ethyl acetate, or acetone - petroleum ether. Solubility in water increases rapidly with temperature.

6.2 Use of adipic acid

The primary use of adipic acid is in the production of nylon 66 polyamide.

6.3 Systems characterisation

The process is modelled theoretically because no production data are available.

6.4 Adipic acid, at plant

6.4.1 Process

Essentially all production of adipic acid is derived from the nitric acid oxidation of a mixture of cyclohexanone – cyclohexanol (KA mixture) which is produced by the oxidation of cyclohexane. The reactor, controlled at 60 – 80 °C and 0.1 – 0.4 MPa, is charged with the recycled nitric acid stream, the KA feed material, and makeup acid containing 50 – 60 % nitric acid and copper – vanadium catalyst. The reaction is very exothermic (6.280 MJ/kg). Adipic acid is obtained in greater than 90 % yield. Nitrogen oxides, carbon dioxide, and some lower dicarboxylic acids are the major by-products, as well as oxidation products arising from impurities in the KA intermediate.

The nitric acid oxidation step produces three major waste streams: an off-gas containing oxides of nitrogen and CO₂, water containing traces of nitric acid and organics from the water removal column; and a dibasic acid purge stream containing adipic, glutaric and succinic acids.

To calculate the amount of KA mixture and nitric acid needed in the production of adipic acid, the following simplified reaction formula is used:



Fig. 6.1 shows the production process.

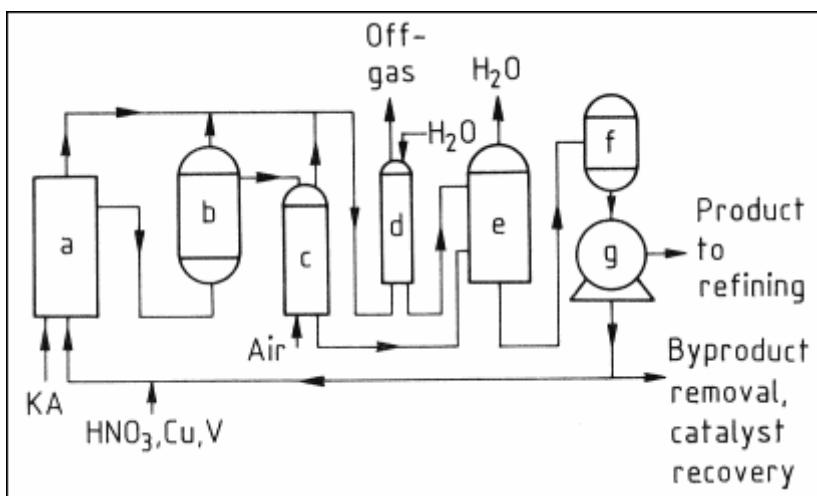


Fig. 6.1 Simplified process of nitric acid oxidation of cyclohexanone -cyclohexanol. (Davis (1997))
A) Reactor, b) Optional cleanup reactor, c) NO₂ bleacher, d) Nitric acid absorber, e) Concentrator, f) Crystal-lizer g) Filter or centrifuge

Fig. 6.2 gives an overview of the in- and output flows and

Tab. 6.2 shows the meta data of the process.

6.4.1.1 Inputs

1.1 mol of KA mixture (cyclohexanol/cyclohexanone = 2/1) and 2 mol of nitric acid are needed per mol adipic acid. Per kg adipic acid (6.843 mol) this corresponds to 0.503 kg cyclohexanol, 0.246 kg cyclohexanone and 0.431 kg nitric acid (100%).

6.4.1.2 Products

Beside the main product, adipic acid, only the di-nitrogen oxide (0.301 kg/kg) is regarded as relevant. The other reaction products are separated and used outside the system boundaries.

6.4.1.3 Process heat

The heat of reaction (6.280 MJ/kg) is more than high enough to provide the energy to heat the inputs to the reaction temperature. Distillation however needs a lot of thermal energy.

6.4.1.4 Electricity

Electricity is used for compressors, fans and pumps. A consumption of 7.95E-4 kWh per kg adipic acid is assumed.

6.4.1.5 Catalysts

The copper and vanadium catalysts are recovered from and reused in the reaction. Because of the presumably very low consumption of the catalyst and because no suitable LCI data are available, the use of catalyst is not taken into account in the LCI.

6.4.2 Emissions

6.4.2.1 Waste heat

The heat of reaction and the electricity consumed are considered as waste heat emissions.

6.4.2.2 Emissions to air

301 g nitrous oxide is produced per kg adipic acid produced. (300 gN₂O/kg according to [Emission inventory Guidebook, B4521-1]). According to EPA⁷, the N₂O emissions from the increasing adipic acid production in the USA have been decreased by 51% since 1990 due to the use of abatement technologies by the 3 major producers (40% of world production). Two of them are using catalytic destruction of N₂O (destruction factor 90 – 95%), the 3rd is using thermal destruction (destruction factor 98 – 99%). (Anonymous (2001))

In this project, we assume that 80% of the N₂O produced in the reaction is destructed by abatement technologies.

6.4.2.3 Emissions to water

The adipic acid contained in waste water is diluted, neutralised, and then degraded biologically. The waste water might be heavy metal contaminated from the catalyst. For the lack of information, no water emissions are taken account of.

6.4.2.4 Emissions to soil

The process induces no direct soil emissions. Indirect emissions (e.g. via waste treatment) are not taken account of.

6.4.2.5 Spent catalysts

The catalyst waste is neglected because the catalyst input is neglected too.

6.4.3 Transport

The standard distances and means of transport from Frischknecht et al. (2007b) are assumed for the transportation of the input materials to the production plant.

6.4.4 Infrastructure

The unspecific chemical production plant is taken into account to consider the infrastructure for the process (cf. part I, Chapter 2.7).

6.5 Data quality considerations

Data are derived from theoretical knowledge of the production process. No measured data have been available.

While the masses of inputs and products are believed to be quite accurate, the energy consumption is a rough estimate. No direct emissions except for N₂O are taken into account. This, of course is an underestimation of them.

⁷ <http://www.epa.gov/globalwarming/emissions/national/n2o.html>, accessed 10.09.2002

Tab. 6.2 Meta data of adipic acid production process

Name	adipic acid, at plant
Location	RER
Infrastructure Process	0
Unit	kg
Data Set Version	2.0
Included Processes	Production including refining (to 99%).
Amount	1
Local Name	Adipinsäure, ab Werk
Synonyms	Hexandisäure
General Comment to reference function	Theoretical data from process analysis. Only the most important flows are taken into account. Energy demand is estimated. More than 80% of the total production is by this process.
CAS Number	124-04-9
Start Date	1997
End Date	2001
Data Valid For Entire Period	1
Other Period Text	
Geography text	
Technology text	Nitric acid oxidation of cyclohexanol / cyclohexanone mixture (2:1) to adipic acid. Abatement of N ₂ O emissions is assumed to reduce the emissions by 80%.
Representativeness [%]	
Production Volume	2.2 million tons per year
Sampling Procedure	Theoretical model
Extrapolations	None

6. Adipic acid

General Flow information				Representation in ecoinvent							Uncertainty information			
Input	Process Name	Output	Remarks	Category	Sub category	Infrastructure	Location	Modul name in ecoinvent	Mean value	Unit	Source mean value	Type	StDv 95%	General Comment
cyclohexanol / cyclohexanone	→	adipic acid, at plant		chemicals	organics	No	RER	cyclohexanol, at plant	7.49E-01	kg	calculated	1	1.45	(4,2,4,2,3,5,3)
nitric acid	→			chemicals	inorganics	No	RER	nitric acid, 50% in H ₂ O, at plant	4.31E-01	kg	calculated	1	1.45	(4,2,4,2,3,5,3)
catalyst	→		not inventoried											
Steam	→			chemicals	organics	No	RER	heat, unspecific, in chemical plant	3.13E+01	MJ	personal communication, M. Overcash	1	1.38	(4,5,2,3,1,5,1)
electricity	→			electricity	production mix	No	UCTE	electricity, medium voltage, production UCTE, at grid	1.06E+00	kWh	personal communication, M. Overcash	1	1.38	(4,5,2,3,1,5,2)
cooling water	→			resource	in water			Water, cooling, unspecified natural origin	1.00E-02	m ³	estimate	1	2.56	(5,5,5,5,5,4)
Transport rail	→		standard distance for raw material transport	transport systems	train	No	RER	transport, freight, rail	7.08E-01	tkm	estimate	1	3.22	(5,5,5,5,5,5)
Transport lorry	→		standard distance for raw material transport	transport systems	road	No	RER	transport, lorry >16t, fleet average	1.18E-01	tkm	estimate	1	3.22	(5,5,5,5,5,5)
Infrastructure (plant) [unite]	→			chemicals	organics	Yes	RER	chemical plant, organics	4.00E-10	unit	estimate	1	4.25	(5,5,5,5,5,9)
	→		Waste heat		air	unspecified		Heat, waste	3.81E+00	MJ	calculated	1	1.38	(4,5,2,3,1,5,14)
	→		H ₂ as byproduct	not inventoried							calculated			
	→		Dinitrogen oxide		air	unspecified		Dinitrogen monoxide	6.02E-02	kg	calculated	1	1.73	(4,2,4,2,3,5,31)
	→		Adipic acid, at plant		chemicals	organics	No	RER	adipic acid, at plant	1.00E+00	kg			

Fig. 6.2 In- and Output flows of the adipic acid production process

6.6 Cumulative Results and Interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

6.7 References

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7 Air Separation

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7.1 Introduction

The main components of air are nitrogen and oxygen, but it also contains smaller amounts of water vapour, argon, carbon dioxide and very small amounts of other gases (e.g. noble gases). The purification and liquefaction of various components of air, in particular oxygen, nitrogen and argon, is an important industrial process.

Nitrogen (N_2) constitutes 78.09% by volume of the air. It is colourless, odourless, and tasteless. Nitrogen is often used as an "inert" gas due to its non-reactive nature with many materials. Commercial nitrogen is produced by different air separation processes as cryogenic liquefaction and distillation, pressure swing adsorption (PSA) and membrane separation.

Oxygen (O_2) constitutes 20.95% by volume of the air. Liquid oxygen is pale blue. The principal use of oxygen stems from its strong oxidising properties. Oxygen is produced by air separation processes that use either cryogenic liquefaction and distillation or separation with vacuum swing adsorption (VSA).

Argon (Ar) is a monatomic, chemically inert gas composing slightly less than 0.93% by volume of the air. Argon is colourless, odourless, tasteless, non-corrosive, non-flammable, and non-toxic. Argon is the most abundant and most used of the noble gases. Commercial argon is the product of cryogenic air separation.

Cryogenic distillation accounts for approximately 85% of nitrogen and over 95% of oxygen production. It is the preferred supply mode for high volume and high purity requirements (Praxair 2002). Cryogenic air separation is currently the most efficient and cost-effective technology for producing large quantities of oxygen, nitrogen, and argon as gaseous or liquid products (Smith & Klosek 2001). Therefore in this inventory only the production of liquefied nitrogen, oxygen and argon by cryogenic air separation was investigated.

The most important physical properties of dry air, oxygen, nitrogen and argon used in this inventory are given in Tab. 7.1.

Tab. 7.1 Physical properties of dry air, oxygen, nitrogen, argon, krypton and xenon

Property	Unit	Air	Oxygen	Nitrogen	Argon
Molecular weight	$g\ mol^{-1}$	28.96	32.00	28.01	39.95
Specific gravity ¹	$kg\ Nm^{-3}$	1.293	1.429	1.250	1.784
Normal boiling point	K	78.9	90.18	77.35	87.28
Specific gravity ²	$kg\ m^{-3}$	874	1141	808.9	1403

¹ At 273.15 K and 0.1013 MPa (Cerbe & Hoffmann 1990)

² At normal boiling point (Flynn 1997)

For the liquefaction process the functional unit is 1 kg of liquefied air in this inventory.

For the allocated products in this inventory, the functional unit is 1 kg of liquefied oxygen, 1 kg of liquefied nitrogen or 1 kg of liquefied argon respectively.

7.2 Reserves and resources of material

Besides the air needed as a resource the major input for the liquefying process is the electricity to compress the inlet air, which normally comprises 95% of the utility costs of a cryogenic air separation plant.

The assessment of the process for Europe gives an uncertainty within the relevant electricity mix. For the unspecified location in Europe (Location: RER) the UCPTE production mix was used. For a specific location, the use of a regional supply mix can lead to large differences in impact due to the different electricity production.

In this inventory the air and its components were not taken into account as a resource. In some plants the amount of processed air (in Nm³) can be up to 5 times larger than the derived liquid products (Cryogenmash 2001). In these plants, the waste gas stream is naturally also much larger (in order to obtain the mass balance).

7.3 Use of material / product

Liquid nitrogen, produced by the cryogenic air separation process, finds wide use as a refrigerant in applications such as cryogenic grinding of plastics and food freezing. Gaseous nitrogen is used in the chemical and petroleum industries for storage tank blanketing and vessel inerting applications, in the food industries to pack oxidisable foods and by the electronics and metals industries for the inert properties.

The major commercial uses of oxygen are in metal manufacturing, metal fabricating, and in health services. Oxygen is also used extensively in the chemical industry and in the pulp and paper industry.

Argon is the most abundant and most used of the noble gases. Its chief use is in metallurgy, where it provides an inert atmosphere in which hot metals can be worked. Because argon is very un-reactive, it prevents chemical reactions of the very hot metal being welded or forged.

7.4 Systems characterization

The production of liquid gases from air was assessed by the process of cryogenic air separation. The process chain was assessed as shown in Fig. 7.1.

The following processes were modelled:

- Cryogenic air separation (Location: RER)
- Allocation of liquefied air to products liquid oxygen, at plant (Location: RER); liquid nitrogen, at plant (Location: RER); liquid argon, crude, at plant (Location: RER)
- Purification of crude argon to: liquid argon, pure, at plant (Location: RER)
- Air separation plant (infrastructure module)

The liquefaction process of air represents an average cryogenic air separation process. For this process, electricity as process energy is needed. Air as main resource for air liquefaction was not accounted as resource because of its inexhaustibility and the short recycling time of the withdrawn products (especially for argon and nitrogen, less for oxygen). A resource of minor importance is cooling water.

As output of the cryogenic air separation liquid air is derived, which is allocated to the three products liquid oxygen, liquid nitrogen and liquid crude argon.

Emissions to the air are already included in the preceding processes especially in the electricity production and are therefore not considered here. The separated CO₂ and water vapour from the separation process were not accounted as emissions. The reason is that these components were already con-

tained in the air input, so that they do not represent effective emissions. The waste heat considered in the liquefaction process is calculated as waste heat of the used electricity only. As wastewater, there is the unevaporated share of the make-up cooling water, but it was not listed because only minor emissions from this source were expected.

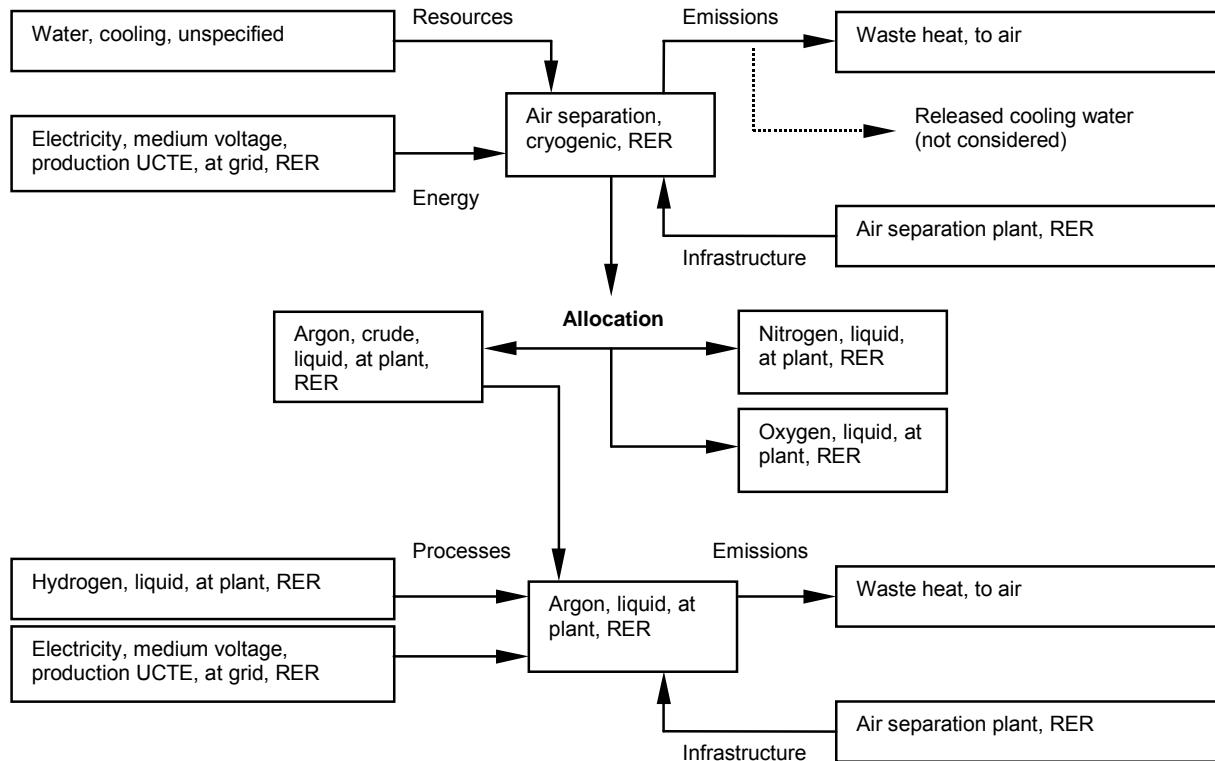


Fig. 7.1 Process chain for the production of liquid oxygen, liquid nitrogen and liquid argon

No transportation process and loss of liquefied gases during storage and transportation was included because the system border is considered at the plant gate and not at the consumer process.

For the transport of liquefied gases to a customer in Switzerland the average distance from the plant to the customer is 150 km. Normally there are two customers serviced with one transport of 10'000 Nm³ liquefied gas ⁸. Therefore a one-way distance for one customer, or per 5'000 Nm³ can be assumed as 100 km.

⁸ Personal communication, Heinz Peyer, Carbagas AG, 2001.

7.5 Air separation, cryogenic

7.5.1 Process

As output of the cryogenic air separation there are three products: liquid oxygen, liquid nitrogen and liquid crude argon. The assumed process includes no gaseous co-products. In reality gaseous products are also processed if there is a demand at the production site. Also the extraction of noble gases from the liquid gases (e.g. Xenon and Krypton from the liquid oxygen) was not considered in this inventory. The investigated cryogenic air separation process leads to liquid products in the following quality:

- Liquid oxygen: min. 99.6 wt-%
- Liquid nitrogen: min. 99.9995 wt-%
- Liquid argon, crude: 96-98 wt-%

An air pre-treatment section downstream of the air compression (0.7 MPa) and after cooling removes process contaminants, including water, carbon dioxide, and hydrocarbons. The air is then cooled to cryogenic temperatures and distilled into oxygen, nitrogen, and, optionally, argon streams. Alternate compressing and expanding the recycled air can liquefy most of it.

Numerous configurations of heat exchange and distillation equipment can separate air into the required product streams. These process alternatives are selected based on the purity and number of product streams, required trade-offs between capital costs and power consumption, and the degree of integration between the air separate unit and other facility units. This process requires very complicated heat integration techniques because the only heat sink for cooling or condensation is another cryogenic stream in the process.

Since the boiling point of argon is between that of oxygen and nitrogen, it acts as an impurity in the product streams. If argon were collected and separated from the oxygen product, an oxygen purity of less than 95% by volume would result (Barron & Randall 1985). On the other hand, if argon were collected with the nitrogen product, the purity of nitrogen would not exceed 98.7% by volume. To achieve higher purities of oxygen and nitrogen the elimination of argon is necessary.

Commercial argon is the product of cryogenic air separation, where liquefaction and distillation processes are used to produce a low-purity crude argon product. Fig. 7.2 gives a simplified scheme of the cryogenic air separation process.

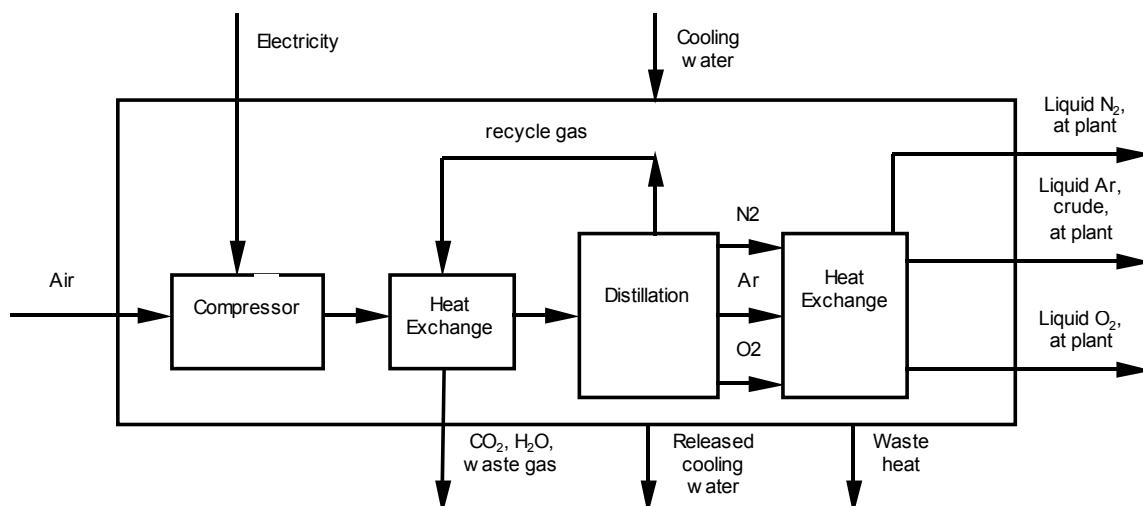


Fig. 7.2 Simplified process of cryogenic air separation

7.5.2 Resources

Electricity

Cryogenic air separation plants require large quantities of electricity. The amount of electricity needed per kilogram of liquefied product depends on the applied process, which is selected based on the purity and number of product streams required.

The specific energy consumptions of gaseous nitrogen generators range from 0.1-0.3 kWh Nm⁻³ depending on capacity and pressure. Producing a liquid product from the distillation system requires 2-3 times the power of producing a gaseous product. The cycle must also efficiently recover the refrigeration contained in the pumped product stream. Plants with nitrogen loops reach a specific energy consumption for liquid nitrogen of 0.8 kWh Nm⁻³. Cold cascades with separate or mixed loops are used in large liquefaction units and have a specific energy consumption for liquid nitrogen of 0.5-0.6 kWh Nm⁻³ (Ullmann 2001, Cap. 4.1).

The value of 0.5 kWh kg⁻¹ for liquid O₂ and N₂ (Frischknecht et al. 1996, Tab. A35.1) bases besides Ullmann on Boustead & Hancock 1979 which presents for liquid nitrogen a value of 0.76 kWh kg⁻¹ and for liquid oxygen values between 0.26 kWh kg⁻¹ and 1.17 kWh kg⁻¹. Some values seem too low and represent rather the production of gaseous nitrogen and oxygen, which has a much lower electricity demand (0.2 kWh kg⁻¹) than the liquid products (Ullmann 2001).

For an ideal process with reversible pre-cooling, the power consumption for air liquefaction would be 0.194 kWh kg⁻¹. The best value obtained lies at 0.8 kWh kg⁻¹ for air liquefaction (Flynn, 1997, p. 322). New production plants need 0.6 kWh kg⁻¹ oxygen⁹. This corresponds approximately to the value for liquefied air at optimal production circumstances of 0.8 kWh Nm⁻³, whereas under non-optimal conditions (part load) the power consumption reaches 1.2 to 1.5 kWh Nm⁻³, which equals 0.9 to 1.2 kWh kg⁻¹ of liquefied product¹⁰. AGA [AGA, 1998 #100] cites the energy consumption for liquid gas production of a modern plant to be slightly below 1 kWh Nm⁻³ (0.77 kWh kg⁻¹). For small plants with a capacity for liquefied products from 1000-6000 kg h⁻¹ the energy consumption was derived from the manufacturers technical data sheets. For these plants the energy consumption lies in a range from 0.7 to 1 kWh per kg of liquefied product (Cryogenmash 2001; Cosmodyne 2001).

An average energy consumption of 0.8 kWh kg⁻¹ liquid air was assumed for this inventory. This value equals the energy consumption of larger plants under average operating circumstances. It covers also the energy consumption of smaller plants under optimal operating circumstances. The lower value (0.5 kWh kg⁻¹) for a large separation plant given by Ullmann 2001 seems very optimistic for a real plant operation. This value was assumed as best case for the power consumption of a large plant. As worst case the value of 1.2 kWh kg⁻¹ was taken, which represents power consumption under unfavourable part load conditions.

For an unspecified location within Europe the UCTE production mix was used. This leads to a high uncertainty when the liquefied air is used for an inventory of a process in a specific location (e.g. food industry in Switzerland). For further precision of the process assessed, the electricity module has to be replaced by a more specific one (local electricity mix). For larger plants with a power consumption of several MW the use of medium voltage electricity is applicable. For small plants also power supply with low voltage (380 V, 50 Hz) would be possible. For this inventory, medium voltage electricity was used, because large plants have the main production share of the liquefied air products in Europe. A summary of the values used is given in Tab. 7.2.

⁹ Personal communication, Nicolas Zennaro, AGA, 2001.

¹⁰ Personal communication, Richard Troxler, Pangas AG Switzerland, 16.01.2002.

Cooling water

The main cooling circuit is assumed as an open recirculating system with a cooling tower. There will be need for replacement of water due to evaporation and blow down.

A small air separation plant (1000-2000 kg d⁻¹) has a cooling water demand (circulating) of 0.12 to 0.16 m³ per kg liquefied product (Cosmodyne 2001). Assumed that the make up of cooling water accounts to 1-3% of the circulating flow (IPPC 2000), the demand for make up water is 1.2-4.8 kg per kg liquefied product. This value is assumed to be valid also for larger plants. According to Recknagel et al. 1997 (p. 1805) a maximal cooling water make up of 3 kg h⁻¹ is necessary to cool 1 kW of generated waste heat. Calculated with the average produced waste heat, a cooling water make up of 2.7 kg per kg of liquefied product would be necessary. This value corresponds to the value calculated from the available plant data. The range of required cooling water make up was assumed to be between 1.2 kg and 4.8 kg per kg of liquefied product.

7.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed is converted to waste heat (2.88 MJ kg⁻¹). In addition, the liquefied gases take up 0.4 MJ kg⁻¹ waste heat. This amount is not considered in the inventory because the cooling ability of the liquid gases in the process where these are used is also not considered (as negative waste heat). The range of waste heat from the electricity use was assumed to be between 1.8 MJ and 4.32 MJ waste heat per kg of liquefied air.

It was assumed that 100% of the waste heat is released to the air mainly through evaporation in the cooling tower.

Emissions to air

The released waste gas containing the unextracted impurities of the air (mainly H₂O and CO₂) and the water vapour of the cooling tower were not counted as emissions (see Section 1.4). No other emissions to the air were considered. The main source of air emissions is the electricity production process.

Wastewater

From the input of cooling water the unevaporated part is released as wastewater. According to the assumptions for the cooling water about 33% of the cooling water make up will be lost due to spray losses (Recknagel et al. 1997, p. 1805). The other 66% will evaporate in the cooling tower. This means that 0.9 kg water per kg of liquefied product will leave the cooling system as wastewater. The values for the assumed range of released wastewater were calculated similarly. The range of wastewater effluents was assumed to be between 0.4 kg and 1.6 kg per kg of liquefied product.

This wastewater contains small amounts of treatment chemicals used for scaling- and fouling inhibition. The water pollution due to the use of these chemicals was not considered in this inventory.

Tab. 7.2 Energy demand, Resource demand and emissions for cryogenic air separation.

Resource, Emission	Unit	per kg liquefied air	Range; per kg liquefied air
Electricity, medium voltage, production UCTE, at grid	kWh	0.8 ¹	0.5 – 1.2
Air (containing N ₂ , O ₂ , Ar) ²	kg	1	
Water, cooling, unspecified natural origin	m ³	2.7 * 10 ⁻³	1.2 * 10 ⁻³ – 4.8 * 10 ⁻³
Waste heat to air ³	MJ	2.88	1.8 – 4.32
Cooling water vapour to air ⁴	kg	1.8	0.8 – 3.2
Wastewater from cooling ⁴	kg	0.9	0.4 – 1.6

Conversion factor from Nm³ to kg for air: 1 Nm³ = 1.293 kg

¹ Assumed as average electricity consumption for a large air separation plant. Value also valid for small air separation plants at optimal operation point (plant size > 1000 kg h⁻¹).

² Air as resource was neglected in the inventory.

³ Only waste heat from electricity use considered. Waste heat from reaction in preceding processes considered.

⁴ Not considered in the inventory. Emissions to water from released cooling water neglected.

7.5.4 Infrastructure

The land use is already included in the infrastructure process of the production facility and therefore not considered separately. The infrastructure of the air separation plant refers to an annual production of 80'000 t liquid product and a plant lifetime of 20 years. Therefore the infrastructure has to be divided by a production of 1.6 Mt. With this product output an infrastructure value of 0.63 * 10⁻⁹ units per kg of liquefied product were calculated.

7.6 Allocated products of cryogenic air separation

An important step in the process chain is the allocation of the burdens on to the products “nitrogen, liquid, at plant”, “oxygen, liquid, at plant” and “argon, crude, liquid, at plant”. For this allocation a plant design without gaseous nitrogen, oxygen or argon products was assumed.

The first step was to determine the necessary amount of energy to liquefy each of the three gases. For this first allocation step it was assumed, that the thermodynamic efficiency of the cooling and liquefying process is for all three gases the same. Therefore the allocation factors were calculated from the heat of vaporisation and the specific heat capacity. In reality there will be some difference in the thermodynamic efficiency for the three gases within the liquefaction process (COP of the compression and expansion cycles). These differences are specific to the used plant design and were neglected in this inventory.

Because in most plants there are possibilities to change the production outputs between nitrogen and oxygen in a wide span, the process output used for the allocation values represent only one possibility. Changes in the proportion of the outputs however do not greatly influence the allocated burdens per kg of product. The calculated difference between the two extreme production modes (max. O₂, and max. N₂) is in the order of 5% of the allocated value.

In the production mode with a maximum liquid O₂ output (around 80 wt-% O₂ of total liquid product) also the liquid argon output reaches a maximum (around 3 wt-% Ar of total liquid product). The liquid N₂ output is the lowest in this mode and the remaining N₂ is released as waste gas or gaseous product, which is not considered in this inventory. In the production mode with a maximum liquid N₂ output (around 90 wt-% N₂ of total liquid product) there is no liquid argon output and the liquid O₂ output reaches a minimum. For this inventory the generated output of liquid oxygen, nitrogen and crude argon (in wt-% of total liquid output) was assumed to be equal to the concentration (by weight) in the

air. This assumed output lies nearer to a possible maximum N₂ output than to a maximum O₂ output of the plant. The calculated allocation factors are presented in Tab. 7.3.

The theoretical energy needed for liquefaction is highest for nitrogen due to the low boiling point and lowest for argon due to the low heat capacity. According to the assumed product output per kg liquefied air (0.231 kg O₂, 0.755 kg N₂, 0.014 kg Ar) the allocation factors calculated from the heat of vaporisation and the specific heat for cooling to the boiling point are 22.2 % for O₂, 76.9 % for N₂, and 0.9 % for Ar. Referred to a liquid output of 1 kg this allocation leads to an electricity consumption of 0.769 kWh for O₂, 0.815 kWh for N₂, and 0.518 kWh for Ar (calculated with a electricity demand of 0.8 kWh per kg of liquefied air). These allocation factors were also applied to the cooling water demand, because the demand of cooling water is linked with the energy demand of the plant. As approximation the same factors were also used to allocate the infrastructure processes.

Tab. 7.3 Calculated allocation factors for liquid air production. Allocation to liquid O₂, N₂ and crude Ar

Liquid gas	L _v ¹	c _p ²	ΔT ³	ΔH	Process output	Allocation factor ⁴	Allocated energy consumption ⁵
	kJ kg ⁻¹	kJ kg ⁻¹ K	K	kJ kg ⁻¹	kg	%	kWh kg ⁻¹
Oxygen	212.9	0.915	202.97	398.58	0.231	22.2	0.769
Nitrogen	198.3	1.039	215.80	422.45	0.755	76.9	0.815
Crude argon	161.6	0.520	205.87	268.71	0.014	0.9	0.518
Total Output	-	-	-	414.92	1.000	100.0	0.800

Process output according to by weight concentration of O₂, N₂ and Ar in the air (100% conversion to liquids).

¹ Heat of vaporization at normal boiling point. Data from Flynn 1997.

² Specific heat capacity c_p at 273 K. Data from Cerbe & Hoffmann 1990; temperature dependence of c_p neglected.

³ Difference between 293 K and boiling point of gas

⁴ Referenced to assumed process output

⁵ Calculated as allocated energy demand per 1kg of liquid output (0.8 kWh per kg energy demand for liquefaction)

7.7 Argon, liquid, pure, at plant

7.7.1 Process

Pure commercial argon (99.999% Ar) is purified from crude argon (96-98% Ar, 2-4% O₂, <1% N₂) in further rectification columns and catalytic removal of the remaining oxygen impurities with hydrogen.

The crude argon is heated in a heat exchanger and compressed to 4-6 bar. Then the deoxygenating of the stream with hydrogen takes place and the stream is cooled from 950 °C to 15 °C. After further cooling in the heat exchanger, pure argon is separated from excess hydrogen in a distillation column.

It is also possible to pass the crude argon through further rectifying columns and achieve an impurity of only 10 ppm without the use of hydrogen¹¹. In this case the consumption of hydrogen would be negligible, but the electricity demand will probably be significant. This alternative purification process was not considered in this inventory. Fig. 7.3 gives a simplified scheme of the purifying process for crude argon.

As resource hydrogen (Process: hydrogen, liquid, at plant, RER) is used to purify the liquefied crude argon. For further compressing, distilling and cooling, electricity (process: electricity, medium voltage, production UCTE, at grid) was used. The transport of the hydrogen to the plant was neglected.

¹¹ Personal communication, Richard Troxler, Pangas AG Switzerland, 16.01.2002.

As output of the purifying unit liquid argon with a purity of 99.999% is derived. The functional unit of the process is 1 kg liquid argon.

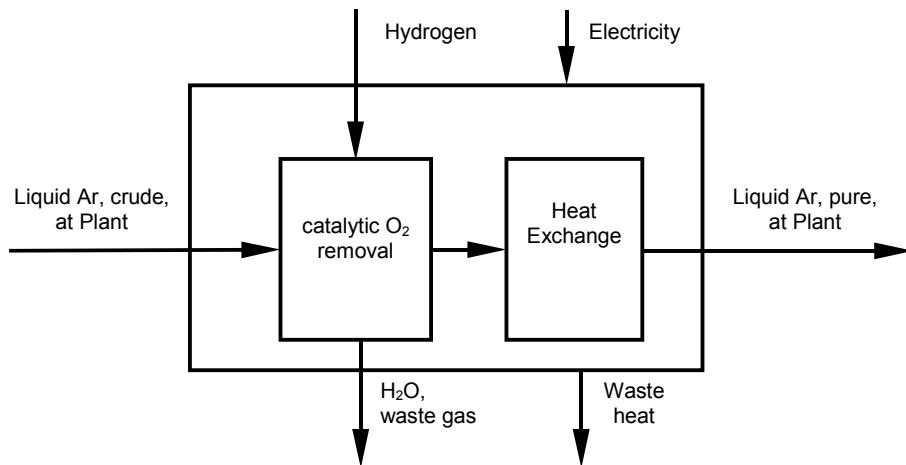


Fig. 7.3 Simplified purification process of crude argon

7.7.2 Resources

Electricity

The energy required for the purification step of crude argon is needed for the catalytic removal of the oxygen impurities and further cooling and distilling of the pure argon. According to Cornelissen & Hirs 1998 the additional energy consumption in the argon purifying unit will be around 0.667 MJ per kg of liquid argon (exergy loss due to the purification step). Thereof 75% or 0.5 MJ kg⁻¹ is needed as hydrogen (gross calorific value) used to remove the oxygen impurities. The remaining 0.167 MJ kg⁻¹ are used for further process steps (compressing, distillation, heat exchanger losses) and are accounted as additional power consumption in this inventory.

Hydrogen

For the purifying of crude argon according to Cornelissen & Hirs 1998 approximately 0.5 MJ hydrogen per kg liquid argon is needed to remove the oxygen impurities. Calculating with a gross calorific value (HHV) of 127.6 MJ per kg hydrogen a demand of 0.004 kg H₂ per kg purified argon was calculated. In Tab. 7.4 a summary of the values used is given.

7.7.3 Emissions

Waste heat

The waste heat considered in this process is calculated as waste heat of the energy used. 100% of the electricity consumed is converted to waste heat. In total there is 0.167 MJ waste heat generated per kg of pure liquid argon. It was assumed that 100% of the waste heat is released to the air. In Tab. 7.4 a summary of the values used is given.

Emissions to air, water

The small amount of waste gas containing mainly H₂O, N₂ and non-oxidized H₂ was neglected. Other emissions to the air and to the water were not considered.

Tab. 7.4 Resources and emissions for argon purification

Resource, emission	Unit	per kg Ar (purified)
Hydrogen, liquid, at plant	kg	0.004
Electricity, medium voltage, production UCTE, at grid	kWh	0.0464
Waste heat, to air	MJ	0.167

²Waste heat from electricity use.

7.7.4 Infrastructure

There was no data on the additional infrastructure demand for the argon-purifying step. For the additional infrastructure needed for this step, 30% of the value of the other liquid products was estimated. With this assumption an infrastructure value of $0.2 * 10^9$ units per kg of purified argon was calculated.

7.8 Air separation plant

7.8.1 Process

The infrastructure of the air separation plant contains besides the aluminium for the column and cold resistant steel for the piping also low-alloyed steel and various other materials in the compressors, cladding and other components. The plant described in this inventory refers to a medium sized plant with an output of 10'000 kg per hour of liquid products (80'000 t per year). Besides the infrastructure in this module also the land use of the plant is included. This module is only a rough approximation for the infrastructure and land use of an air separation plant. The process chain was assessed as shown in Fig. 7.4.

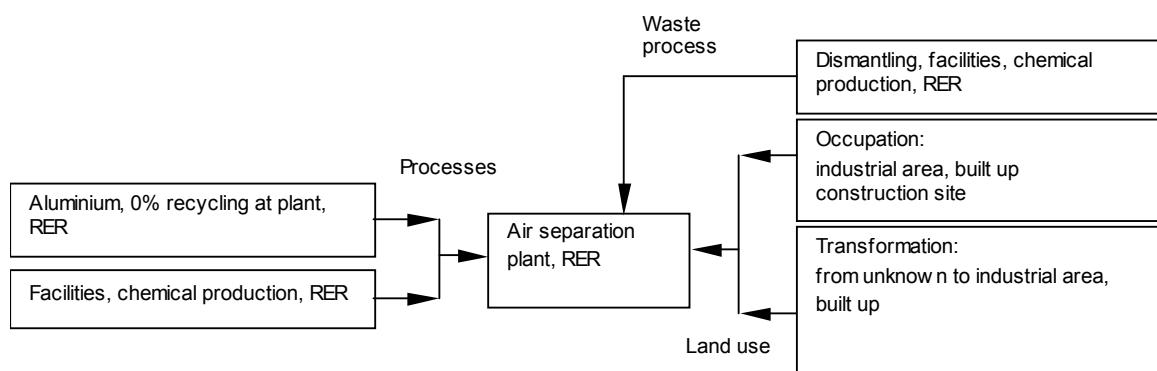


Fig. 7.4 Process chain for the infrastructure of an air separation plant

7.8.2 Land use and infrastructure

Infrastructure

The infrastructure of the air separation plant contains besides cold resistant steel and aluminium for the piping and the column also low-alloyed steel and various other materials in the compressors and other components. The weight of the equipment is largely dependent of the size of the plant. For small plants with an output of 100 kg liquefied product per hour a plant weight of 8-10 t is common (Stirling 2002). For very large plants the specific weight (referred to the output per hour) of the plant is estimated to be more than 10 times smaller (Messer Griesheim 2000). For this inventory an amount of 10 kg per kg hourly production output was assumed. This leads to a total plant weight of 100 t. 10% of the total weight was accounted as aluminium for the column. The rest was assumed to be a similar material composition as used for the production facilities in the chemical industry. This amount was assessed with the process “facilities, chemical production”. In this process the transports to the construction site are already included. For the aluminium used in the construction the standard distances for Europe of 200 km rail (2000 tkm) and 100 km road (1000 tkm, lorry 32 t) were applied for these transports.

For the disposal it was assumed that the aluminium column is recycled and therefore no disposal process was included for this part. For the rest of the plant the process “Dismantling, facilities, chemical production” was applied. The values used for the infrastructure are given in Tab. 7.5.

Land use

Also the land use of the air separation plant depends on the size of the plant. For small plants with an output of 100 kg liquefied product per hour a space requirement of 0.3 m² per kg hourly production is reported (Stirling 2002). For larger plants with an output of 3000 kg liquefied product per hour the space requirement lowers to 0.2 m² per kg hourly production (Cosmodyne 2001). For very large plants the land use was estimated to be about 0.1 m² per kg hourly production. For this inventory an average amount of 0.1 m² per kg hourly production output was assumed. This leads to a total area occupied by the plant of 1000 m². The whole site was accounted as “industrial area, built up”. For the time of occupation 20 years were assumed as plant lifetime. Furthermore, one year of occupation as construction site for construction and dismantling was assumed. The occupation of the area before the occupation as industrial area is not known (transformation from unknown). The values used for the infrastructure are given in Tab. 7.5.

Tab. 7.5 Land use and infrastructure of the air separation plant.

Resource, Use	Unit	per unit ¹	per kg of product
Aluminium, 0% recycling	kg	$10 * 10^3$	$6.25 * 10^{-6}$
Facilities, chemical production	kg	$90 * 10^3$	$56.3 * 10^{-6}$
Dismantling, facilities, chemical production	kg	$90 * 10^3$	$56.3 * 10^{-6}$
Transport, freight, rail, RER	tkm	$2 * 10^3$	$1.25 * 10^{-6}$
Transport, lorry 32t, RER	tkm	$1 * 10^3$	$0.625 * 10^{-6}$
Occupation, industrial area, built up	m ² a	$20 * 10^3$	$12.5 * 10^{-6}$
Occupation, construction site	m ² a	$1 * 10^3$	$0.625 * 10^{-6}$
Transformation, from unknown	m ²	$1 * 10^3$	$0.625 * 10^{-6}$
Transformation, to industrial area, built up	m ²	$1 * 10^3$	$0.625 * 10^{-6}$

¹ Air separation plant with a liquid product output of 0.08 Mt a⁻¹ or 0.8 Mt during the whole lifetime (20 years) of the site. Per kg of liquid product therefore a share of $625 * 10^{-12}$ units of the infrastructure is needed.

7.9 Data quality considerations

Tab. 7.6 shows the data quality indicators for the inventory of liquefied gas production in Europe (oxygen, nitrogen, argon). Tab. 7.8 shows the data quality indicators for the inventory of pure argon production. Tab. 7.9 shows the data quality indicators for the infrastructure of the air separation plant. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The most important data for the production of liquefied gases is the electricity demand. This data was derived from different sources and shows a quite large range depending on plant size and production mode. The used electricity mix refers to an average European production. Therefore for a specific location of the air separation plant large differences may occur when using a local supply mix.

The allocation used is based on a theoretical (ideal) energy demand for cooling and liquefaction of the gases. The uncertainty in using those and not other (more specific) allocation rules is of importance but cannot be quoted as a data uncertainty. The allocation factors used for the three gases are shown in Tab. 7.7.

The cooling water demand is based on assumptions concerning the operation of the cooling circuit and has therefore higher uncertainties. The highest uncertainties exist for the data concerning the argon purifying. Depending on the process used in a plant and the purity required the amount of energy and hydrogen may vary largely.

In general the infrastructure data has a high uncertainty: Because of missing specific data approximations were used in this inventory. Especially uncertain is the infrastructure for the argon-purifying step, which was only roughly estimated.

Tab. 7.6 In- / Outputs for the module “air separation, cryogenic, at plant”, location RER

Process output: 1 kg, air separation, cryogenic, RER		Value	Unit	Uncertainty			Comment
Name, Location	Type			Score	St.Dev.		
electricity, medium voltage, production UCTE, at grid, UCTE air separation plant, RER	8.00E-1 kWh	lognorm	3.4,1,1,1,4	1.19E+0	Data from different sources and literature		
Water, cooling, unspecified natural origin	6.30E-10 unit	lognorm	5.5,1,3,3,5	3.36E+0	Estimated from data of small plants		
Heat, waste, to air, low population density	2.70E-3 m³	lognorm	3.4,1,1,4,4	1.55E+0	Assumptions of technology used for cooling		
oxygen, liquid, at plant, RER	2.88E+0 MJ	lognorm	3.4,1,1,1,4	1.19E+0	Calculated from electricity use		
nitrogen, liquid, at plant, RER	2.31E-1 kg	- not applicable			- Uncertainty not applicable for allocated product		
argon, crude, liquid, at plant, RER	7.55E-1 kg	- not applicable			- Uncertainty not applicable for allocated product		
Allocated amount	1.40E-2 kg	- not applicable			- Uncertainty not applicable for allocated product		

(1) From technosphere; 2) Ressources; 3) Emissions; 4) Products of multi output process

Tab. 7.7 Allocation factors used for products “oxygen, liquid”, “nitrogen, liquid”, “argon, crude, liquid”

Allocation factor for products of cryogenic air separation: oxygen, liquid; nitrogen, liquid; argon, crude, liquid; at plant, RER		Unit	Allocation factor used			Comment
Name, Location	Type		Oxygen	Nitrogen	Argon	
electricity, medium voltage, production UCTE, at grid, UCTE air separation plant, RER	%	22.2	76.9	0.9		The allocation factors were calculated from the heat of vaporisation and the specific heat capacity multiplied with the temperature difference from 20°C to the boiling point.
Water, cooling, unspecified natural origin	%	22.2	76.9	0.9		
Heat, waste, to air, low population density	%	22.2	76.9	0.9		
Allocated amount	kg	2.31E-1	7.55E-1	1.40E-2		Product output according to concentration in air

(1) From technosphere; 2) Ressources; 3) Emissions; 4) Products of multi output process

Tab. 7.8 In- / Outputs for the module “argon, liquid, at plant”, location RER

Process output: 1 kg, argon, liquid, at plant, RER			Uncertainty			Comment
Name, Location	Value	Unit	Type	Score	St.Dev.	
= electricity, medium voltage, production UCTE, at grid, UCTE	4.64E-2	kWh	lognorm	4,5,1,3,5,5	2.15E+0	Data from 1 literature reference estimated
	4.00E-3	kg	lognorm	4,5,1,3,5,5	2.15E+0	Data from 1 literature reference estimated
	1.03E+0	kg	lognorm	not applicable	1.02E+0	Calculated from Ar concentration of 97%, Value set to 1.02
	2.00E-10	unit	lognorm	5,5,1,3,5,5	4.00E+0	Rough estimate
Heat, waste, to air, low population density	1.67E-1	MJ	lognorm	4,5,1,3,5,5	2.15E+0	Calculated from electricity use
1) From technosphere; 2) Emissions						

Tab. 7.9 In- / Outputs for the module “air separation plant”, location RER

Process output: 1 unit, air separation plant, RER			Uncertainty			Comment
Name, Location	Value	Unit	Type	Score	St.Dev.	
= aluminium, primary, at plant, RER	1.00E+4	kg	lognorm	5,5,1,3,3,5	1.68E+0	Estimated from data of small plants
	9.00E+4	kg	lognorm	5,5,1,3,3,5	3.36E+0	Estimated from data of small plants
	9.00E+4	kg	lognorm	5,5,1,3,3,5	3.36E+0	Estimated from data of small plants
	2.00E+3	tkm	lognorm	4,5,nA,nA,nA,nA	2.09E+0	Estimated with standard distances for Europe
= transport, lorry 32t, RER	1.00E+3	tkm	lognorm	4,5,nA,nA,nA,nA	2.09E+0	Estimated with standard distances for Europe
Occupation, industrial area	2.00E+4	m2a	lognorm	4,5,1,3,3,5	1.73E+0	Estimated from data of small plants
Occupation, construction site	1.00E+3	m2a	lognorm	4,5,1,3,3,5	1.73E+0	Estimated from data of small plants
Transformation, from unknown	1.00E+3	m2	lognorm	4,5,1,3,3,5	2.19E+0	Estimated from data of small plants
Transformation, to industrial area, built up	1.00E+3	m2	lognorm	4,5,1,3,3,5	2.19E+0	Estimated from data of small plants
1) From technosphere; 2) Ressources						

7.10 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

7.11 Conclusions

The production of liquefied gases is determined largely by the impact of the electricity used. For further precision of the data it would be necessary to divide the process into processes with different plant sizes and main output products. Also the source mix of the electricity production should be adapted to the specific location of the inventory.

In the data used for this inventory the allocation between liquid and gaseous outputs are not stated. For the calculation of the allocation factors it was assumed that no gaseous product is desired and therefore only liquid outputs are accounted. For the use of pure gaseous nitrogen and oxygen the production energy needed is much smaller (in order of 0.1-0.3 kWh per Nm³). In future work, modules should be provided also for gaseous products, as used, e.g., in steel production.

7.12 References

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8 Alkyds

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8.1 Introduction

Alkyd resins are polyesters made by the polymerisation of three types of monomers:

1. Polyols
2. Polybasic acids
3. Fatty acids or triglyceride oils

Because of the distinctive properties, alkyd resins often are classified separately from other polyesters.

Terminology relating to alkyd resins has changed considerably over the years and thus can be confusing. The ASTM defines an alkyd as "a synthetic resin made from polyhydric alcohols and polybasic acids; generally modified with resins, fatty oils, or fatty acids". For this LCI the slightly narrower and more exact definitions from (Jones (1997)) have been adopted:

Tab. 8.1 Definition of alkyd resins (Jones (1997))

Types of monomer	Terminology		
Polyols			
Polybasic acids	{ Polyester resins	{ Alkyd resins	{ Modified alkyd resins
Fatty acids			
Others			

The most common polyol and polybasic acid used for alkyd resin production are glycerol and phthalic anhydride.

Because alkyd resins are a large and diverse family, several sub-classifications often are used.

There are two broad groupings according to the fatty acid type.

1. Drying alkyds contain enough unsaturated fatty acids to make curing by oxygen possible.
2. Non-drying alkyds contain lower levels of unsaturated fatty acids and are not polymerised appreciably with oxygen.

Another classification called "oil length" groups alkyd resins by the amount of oil or fatty acid present, as follows:

Tab. 8.2: „Oil length classification of alkyd resins according to (Jones (1997))

Oil length	% Oil or fatty acids	Typical use
Short oil alkyd	35–45	Industrial stoving finishes, wood paints (combined with other resins)
Medium oil alkyd	46–55	Industrial coatings
Long oil alkyd	56–70	Architectural paints
Very long oil alkyd	> 70	Architectural paints

Alkyd paints are basically composed of alkyd resin, solvent, pigments, additives such as wetting, anti-settling and anti-skimming agents and dryers.

Water-borne alkyd paints for architectural use are emulsions with a solids content of 40 – 60%. The size of the emulsified particles is in the range of 5 – 15 µm. The content of emulsifiers has to be kept low to obtain good water resistance and drying behaviour. (Küchenmeister (1997))

Solvent-born long oil alkyd paints most commonly use white spirit (mineral spirit) as solvent. Solids contents may reach 80%. The concentrated resin solution is further diluted to bring the paint in a ready-for-use state. (Küchenmeister (1997))

8.2 Use of alkyds

The largest use of alkyds (>95%) is for surface coatings (paints, enamels, lacquers, and varnishes) in which the resins function as binders. Alkyd resins account for ca. 45% of the global paint raw material production. These are very versatile coating binders, and are used extensively in architectural, industrial, and special purpose coatings. It is estimated that about one third of all organic coatings applied world-wide use alkyds as a primary binder, and perhaps another one fourth of all coatings contain smaller amounts of alkyds. (Jones (1997))

8.3 Alkyd resin, long oil, 70% in white spirit, at plant

8.3.1 Solvent process

Alkyd resin is produced in a condensation polymerisation. The water generated in this reaction has to be removed because the esterification reaction is highly reversible. In commercial processes this is usually done by adding a few percent of un-reactive, water-immiscible solvent (usually xylene) to the formulation. Tab. 8.3 gives the material in- and outputs for a „typical“ long oil alkyd resin and Fig. 8.1 shows a possible reactor configuration. The stirred alkyd polymerisation mass will boil vigorously at about 250 °C. The xylene vapours form an azeotrope with water and carry it out of the reactor through a "partial condenser" usually operated at about 100 °C. Thus water vapour escapes, but most of the xylene and almost all of the monomers condense and are returned to the reactor.

For the mass flows the information from (Jones (1997)) is used while the energy consumption given in (von Däniken & Chudacoff (1995)) is adjusted to the functional unit in this LCI. No specific data are available for the heat energy generation. Therefore the unspecific heat production in chemical plants is used. No information was found about the inert gas input that can be expected from Fig. 8.1.

Fig. 8.2 gives an overview of the in- and output flows and Tab. 8.4 shows the meta data of the process.

8.3.2 Waste / Emissions

8.3.2.1 Waste heat

The heat of the electricity consumed is considered as waste heat emission to air.

8.3.2.2 Liquid / solid waste

The liquid and solid organic waste of the process is assumed to be burned for heat generation and thus is not balanced.

8.3.2.3 Emissions to air

The VOC emissions of the process are assumed to be burned for heat generation and thus are not balanced.

8.3.2.4 Emissions to water

There are no emissions to water from the process. The reaction water is removed as steam. Eventual water emissions from cleaning etc. are not considered.

8.3.2.5 Emissions to soil

The process induces no direct soil emissions. Indirect emissions (e.g. via waste treatment) are not taken account of.

8.3.3 Transport

The standard distances and means of transport (Frischknecht et al. 2003) are assumed for the transportation of the input materials to the production plant.

8.3.4 Infrastructure

The unspecific chemical production plant is taken into account to consider the infrastructure for the process (cf. part I, Chapter 2.7).

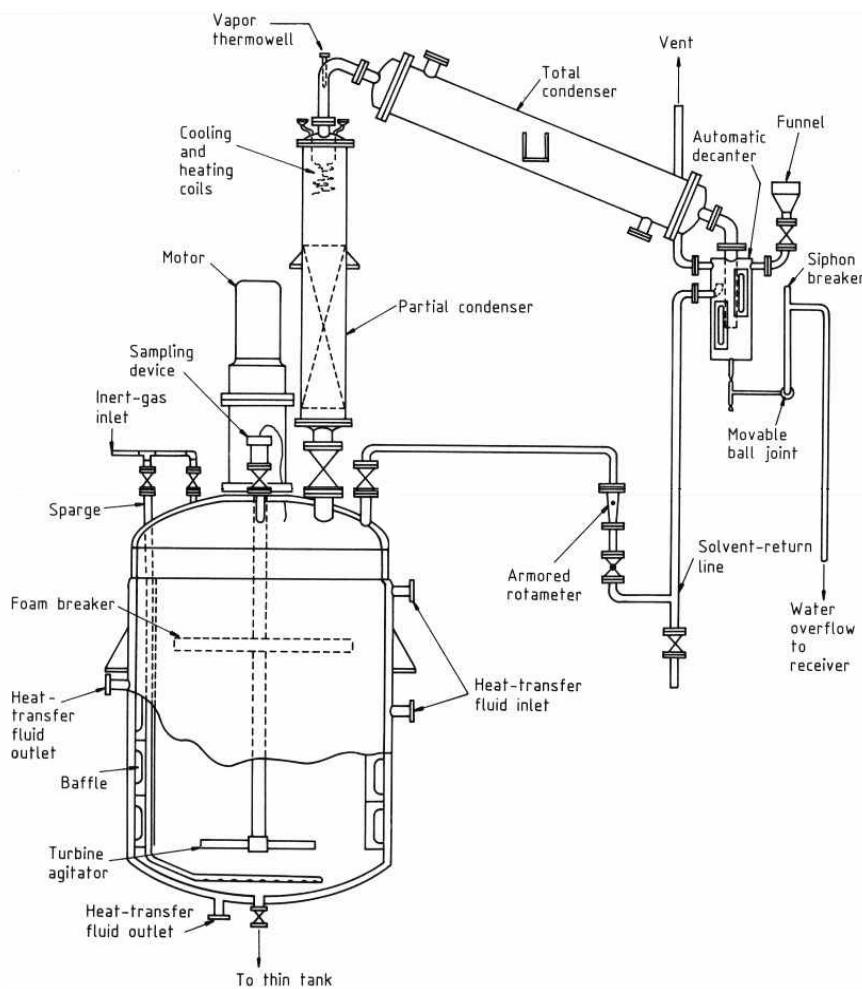


Fig. 8.1 Reactor and overhead for alkyd resin production (Jones (1997))

Tab. 8.3: Inputs and products for a typical long oil alkyd resin in white spirit (70% resin w/w)

	(Jones (1997)): Data per 0.582 kg alkyd resin (100% yield)	calculated from (Jones (1997)) per kg resin in white spirit (incl. white spirit)	calculated from (Jones (1997)) per kg "alkyd resin, 70% in white spirit"-output	(von Däniken & Chudacoff (1995)): Data per kg resin in white spirit (incl. white spirit)	Used for 1 kg "alkyd resin, long oil, 70% in white spirit, at plant"
Soybean fatty acid [kg]	0.349	0.631	0.442	0.460	0.631
Pentaeritol [kg]	0.126	0.227	0.159	0.142	0.227
Phthalic anhydride [kg]	0.148	0.268	0.187	0.153	0.268
Theoretical yield of resin [kg]	0.582	1.053	0.737	-	1.053
Practical yield of resin (yield factor: 0.95) [kg]	-	1.000	0.700	-	1.000
Xylene (4% of polymerisation mass) [kg]	-	0.045	0.032	-	0.045
White Spirit [kg]	-	0.429	0.300	0.280	0.429
Electricity [kWh/kg]				0.015	0.021
Heat energy [MJ/kg]				3.110	4.443
Water [kg]	0.040	0.073	0.051	-	0.073
Xylene (0.97 returned to the reactor) [kg]	-	0.044	0.031	-	0.044
Waste / Emissions (from mass balance) [kg]	-	0.054	0.038	-	0.054
Total Product (alkyd resin, 70% in white spirit, incl. solvent) [kg]	-	1.429	1.000	1.000	1.429

The output "Waste / Emissions" is not inventoried as such (details see 8.3.2). The reference function is the alkyd resin without the solvent. Therefore the product output including the solvent is more than 1 kg

Tab. 8.4 Meta data of the production process of long oil alkyd resin in white spirit (70% w/w)

Name	alkyd resin, long oil, 70% in white spirit, at plant
Location	RER
Infrastructure Process	0
Unit	kg
Data Set Version	2.0
Included Processes	Transport of raw materials and production of resin. Packaging is neglected.
Amount	1
Local Name	Alkydharz langölig, 70% in Reinbenzin, ab Werk
Synonyms	
General Comment to reference function	Alkyds are a large and diverse family of polyesters. Long oil alkyds are often used in architectural paints. This dataset stands for one specific long oil alkyd and should not be used for other alkyds if its contribution to the overall result is important. The data quality is not sufficient to allow for e.g. a comparative assessment of different binders of paints.
CAS Number	
Start Date	1995
End Date	2001
Data Valid For Entire Period	1
Other Period Text	
Geography text	
Technology text	The dataset models the commonly used solvent process. It assumes the use of soybean oil as fatty acid, phthalic anhydride as polybasic acid and Pentaeritol as polyol.
Representativeness [%]	
Production Volume	Unknown
Sampling Procedure	A "typical" alkyd is chosen and its raw material consumption is calculated. Energy data are taken from the one source that is known.
Extrapolations	None

General Flow information				Representation in ecoinvent							Uncertainty information				
Input	Process Name	Output	Remarks	Category	Sub category	Infrastructure	Location	Modul name in ecoinvent	Mean value	Unit	Source mean value	Type	StDv 95%	General Comment	
Soybean fatty acid	→			chemicals	organics	No	RER	soya oil, at plant	6.31E-01	kg	Jones 1997	1	1.73	(4,5,5,2,3,5,3)	
Pentaeritol	→			chemicals	organics	No	RER	penta-erythritol, at plant	2.27E-01	kg	Jones 1997	1	1.73	(4,5,5,2,3,5,3)	
Phthalic anhydride	→			chemicals	organics	No	RER	phthalic anhydride, at plant	2.68E-01	kg	Jones 1997	1	1.73	(4,5,5,2,3,5,3)	
Xylene	→			4% of polymerisation mass	chemicals	organics	No	RER	xylene, at plant	4.50E-02	kg	Jones 1997	1	1.73	(4,5,5,2,3,5,3)
White Spirit	→				paintings	production	No	RER	white spirit, at plant	4.29E-01	kg	calculated	1	1.73	(4,5,5,2,3,5,3)
Transport rail	→		standard distance for raw material transport	transport systems	train	No	RER	transport, freight, rail	9.60E-01	tkm	estimate	1	3.22	(5,5,5,5,5,5)	
Transport lorry	→		standard distance for raw material transport	transport systems	road	No	RER	transport, lorry >16t, fleet average	1.60E-01	tkm	estimate	1	3.22	(5,5,5,5,5,5)	
Electricity [kWh/kg]	→			electricity	production mix	No	UCTE	electricity, medium voltage, production UCTE, at grid	2.14E-02	kWh	von Däniken & Chudacoff 1995	1	1.29	(3,4,3,3,3,1,2)	
Heat energy [MJ/kg]	→			chemicals	organics	No	RER	heat, unspecific, in chemical plant	4.44E+00	MJ	von Däniken & Chudacoff 1995	1	1.29	(3,4,3,3,3,1,1)	
Infrastructure (plant)	→			chemicals	organics	Yes	RER	chemical plant, organics	4.00E-10	unit	estimate	1	4.25	(5,5,5,5,5,9)	
	→	waste heat		air	unspecified			Heat, waste	7.71E-02	MJ	calculated	1	1.29	(3,4,3,3,3,1,14)	
	→	water	as steam to air --> not inventoried						7.31E-02	kg	calculated				
	→	xylene recovered	not inventoried						4.37E-02	kg	estimate				
	→	other outputs	recycled as fuel --> not inventoried						5.40E-02	kg	calculated				
	→	Alkyd resin	weight including solvent = 1.43 kg	paintings	production	No	RER	alkyd resin, long oil, 70% in white spirit, at plant	1.00E+00	kg					

Fig. 8.2 In- and Output flows of the production process of long oil alkyd resin in white spirit (70% w/w)

8.4 Alkyd paint, white, 60% in solvent, at plant

8.4.1 Production

The paint is produced by physical mixing the alkyd resin with the pigments, auxiliary products and the solvent (white spirit). The raw materials needed are calculated from a typical composition of a solvent-borne white paint.

The type and amount of the pigments used depends on the colour of the paint. Inorganic pigments usually are metal oxides. Metals like Fe, Cr, Al, Ti, Zn, Mo, Pb and even Cd are used. The most important organic pigments are the azo pigments but the metal-complex pigments are also widely used.

White paint usually uses TiO_2 , which probably is one of the more environmental friendly pigments.

8.4.2 Inputs

Since the alkyd resin solution in ecoinvent already contains some solvent (white spirit), the solvent input necessary to reach the solvent content in the paint is calculated as the difference of the amount of solvent in the paint minus the amount of solvent in the resin. (see Tab. 8.5). The yield of the process is 98.5% (see 8.4.3).

Tab. 8.5 Input of raw materials for solvent-born paint production

	Composition of paint (Streitberger (1997))	Composition of alkyd resin solution in ecoinvent	Input of raw materials¹⁾
Solid content	60%		
Alkyd resin solution			41%
Alkyd resin	29%	70%	
Pigment	30%		30%
Auxiliaries	1%		1%
Solvent (white spirit)	40%	30%	28%

1 kg "alkyd resin ... in white spirit" in ecoinvent corresponds to 1.43 kg alkyd resin solution. Thus only 0.7 times the amount of alkyd resin solution is inventoried as "alkyd resin ... in white spirit".

Beside the material inputs, electricity for the pumps, mills and mixers is needed. It is assumed that twice the amount consumed in the resin fabrication, i.e. 0.0428 kWh/kg is needed.

Fig. 8.3 gives an overview of the in- and output flows and Tab. 8.6 shows the ecoinvent meta data of the process.

8.4.3 Waste / Emissions

8.4.3.1 Waste heat

The heat of the electricity consumed is considered as waste heat emission to air.

8.4.3.2 Liquid / solid waste

It is assumed that 1% of the material input has to be disposed as waste.

8.4.3.3 Emissions to air

It is assumed that 1% of the total solvent evaporates to air.

8.4.3.4 Emissions to water

There are no emissions to water from the process.

8.4.3.5 Emissions to soil

The process induces no direct soil emissions. Indirect emissions (e.g. via waste treatment) are not taken account of.

8.4.4 Transport

The standard distances and means of transport (Frischknecht et al. 2003) are assumed for the transportation of the input materials to the production plant.

8.4.5 Infrastructure

The unspecific chemical production plant is taken into account to consider the infrastructure for the process (cf. part I, Chapter 2.7).

Tab. 8.6 Meta data of the production process of alkyd paint, white, 60% in solvent, at plant

Name	alkyd paint, white, 60% in solvent, at plant
Location	RER
Infrastructure Process	0
Unit	kg
Data Set Version	2.0
Included Processes	Transport of raw materials and production of paint. Packaging is neglected.
Amount	1
Local Name	Alkydharzlack, weiss, 60% in Lösemittel, ab Werk
Synonyms	
General Comment to reference function	Alkyd paints can be made of many different resins. This dataset stands for one specific long oil alkyd as used in architectural paints of white colour and should not be used for other alkyds if its contribution to the overall result is important. The data quality is not sufficient to allow for e.g. a comparative assessment of different paints.
CAS Number	
Start Date	1995
End Date	2001
Data Valid For Entire Period	1
Other Period Text	
Geography text	
Technology text	Physical mixing of inputs.
Representativeness [%]	
Production Volume	Unknown
Sampling Procedure	A "typical" solvent-borne white alkyd paint is chosen and its raw material consumption is calculated. Energy data are estimated.
Extrapolations	None

General Flow information				Representation in ecoinvent							Uncertainty information				
Input	Process Name	Output	Remarks	Category	Sub category	Infrastructure	Location	Modul name in ecoinvent	Mean value	Unit	Source mean value	Type	StDv 95%	General Comment	
Alkyd resin, in solution	→	alkyd paint, white, 60% in solvent, at plant	weight including solvent = 0.42 kg	paintings	production	No	RER	alkyd resin, long oil, 70% in white spirit, at plant	2.94E-01	kg	calculated	1	1.73	(4,5,5,2,3,5,3)	
Pigment	→			chemicals	inorganics	No	RER	titanium dioxide, production mix, at plant	3.05E-01	kg	calculated	1	1.73	(4,5,5,2,3,5,3)	
Auxiliaries	→			chemicals	organics	No	GLO	chemicals organic, at plant	1.02E-02	kg	calculated	1	1.73	(4,5,5,2,3,5,3)	
Solvent	→			paintings	production	No	RER	white spirit, at plant	2.80E-01	kg	calculated	1	1.73	(4,5,5,2,3,5,3)	
Transport rail	→			standard distance for raw material transport	transport systems	train	No	RER	transport, freight, rail	6.09E-01	tkm	estimate	1	3.22	(5,5,5,5,5,5)
Transport lorry	→			standard distance for raw material transport	transport systems	road	No	RER	transport, lorry >16t, fleet average	1.02E-01	tkm	estimate	1	3.22	(5,5,5,5,5,5)
Electricity	→			waste heat	air	unspecified			electricity, medium voltage, production UCTE, at grid	4.28E-02	kWh	estimate	1	1.93	(5,5,5,2,3,5,2)
Infrastructure (plant)	→			solvent to air	air	unspecified			chemical plant, organics	4.00E-10	unit	estimate	1	4.25	(5,5,5,5,5,9)
	→			waste to treatment	waste management	hazardous waste incineration	No	CH	Heat, waste	1.08E-01	MJ	calculated	1	1.93	(5,5,5,2,3,5,14)
	→			solventborne alkyd paint	paintings	production	No	RER	Hydrocarbons, aliphatic, alkanes, unspecified disposal, paint remains, 0% water, to hazardous waste incineration	4.00E-03	kg	estimate	1	3.22	(5,5,5,5,5,23)
									alkyd paint, white, 60% in solvent, at plant	1.10E-02	kg	estimate	1	2.56	(5,5,5,5,5,6)
										1.00E+00	kg				

Fig. 8.3 In- and Output flows of the production process of alkyd paint, white, 60% in solvent, at plant

8.5 Alkyd paint, white, 60% in water, at plant

8.5.1 Production

To make alkyd resins miscible with blends of water and organic solvent it is necessary to attach hydrophilic sites to the polymer molecule. The most common way to do so is to place acidic carboxy groups on the molecule and then to "salt" the resin with a base, usually ammonia or an amine. A representative method using a two-stage process involving trimellitic anhydride is shown in Fig. 8.4. Other ways are to copolymerise hydrophilic polyethylene oxide segments into the resin, to emulsify hydrophobic alkyds with conventional surfactants, and to prepare transparent micro-emulsions. (Jones (1997))

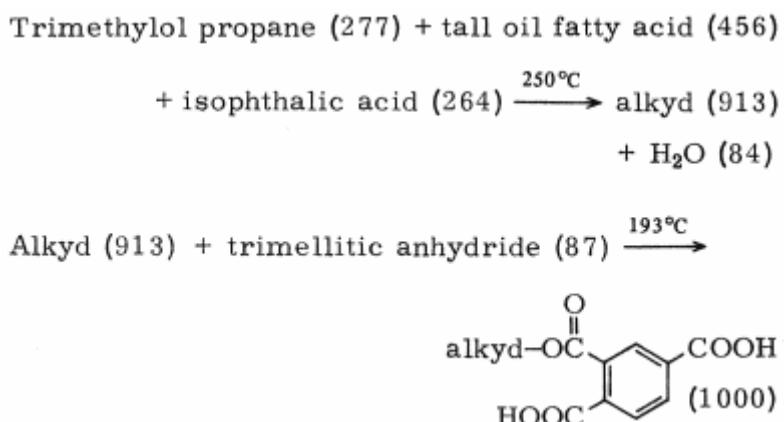


Fig. 8.4 Production of water-reducible alkyd resins (mass part in parenthesis) (Jones (1997))

- Trimethylol propane ($\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{OH})_3$) is a colourless, crystalline, trivalent alcohol, made by the base-catalyzed aldol addition of butyraldehyde with formaldehyde followed by Cannizzaro reaction of the intermediate 2,2-bis(hydroxymethyl)butanal with additional formaldehyde and at least a stoichiometric quantity of base.
- Tall oil is a by-product of the Kraft process for pulping softwoods (paper production). The tall oil fatty acids, primarily C_{18} types, are similar in composition to those derived from soybean oil.
- Phthalic acid ($\text{C}_8\text{H}_6\text{O}_4$) is formed as a by-product in the manufacture of phthalic anhydride. It forms colourless, monoclinic crystals that melt at ca. 210°C and are converted into phthalic anhydride with the elimination of water.
- The preparation of trimellitic anhydride ($\text{C}_9\text{H}_4\text{O}_5$) is best achieved by the liquid-phase catalytic oxidation of 1,2,4-trimethylbenzene (pseudocumene) with air.

The paint is produced by physical mixing the water-reducible alkyd resin with the pigments, auxiliary products and water. The raw materials needed are calculated from a typical composition of a solvent-borne white paint.

The type and amount of the pigments used depends on the colour of the paint. Inorganic pigments usually are metal oxides. Metals like Fe, Cr, Al, Ti, Zn, Mo, Pb and even Cd are used. The most important organic pigments are the azo pigments but the metal-complex pigments are also widely used.

White paint usually uses TiO_2 , which probably is one of the more environmental friendly pigments.

8.5.2 Inputs

The material inputs for the production of water-reducible alkyd resin are inventoried according to the information in Fig. 8.4. The inputs are normalised to 1 kg assuming yield of 95%. The resin is mixed with the amount of water necessary to increase the water content to 40%. The material inputs are shown in Tab. 8.7.

Tab. 8.7 material inputs for the production of water-reducible alkyd paint

Preparation of water-reducible alkyd resin			Preparation of alkyd paint, 60% in water		
	Amount [% (w/w)]	[kg/kg paint]		Amount [% (w/w)]	[kg/kg paint]
Inputs			Inputs		
trimethylol propane	25.55%	0.0835	alkyd resin	28.00%	0.2828
tall oil fatty acid	42.07%	0.1374	pigment	30.00%	0.3030
isophthalic acid	24.35%	0.0795	auxilaries	2.00%	0.0202
trimellitic anhydride	8.03%	0.0262	water	40.00%	0.3766
Output			Output		
alkyd resin	86.60%	0.2828	alkyd paint	99.00%	1.0000
water	8.40%	0.0274	waste	1.00%	0.0101
waste	5.00%	0.0163			

Beside the material inputs, electricity for the pumps, mills and mixers is needed. It is assumed that the amount consumed corresponds to the amount consumed in the solvent-borne resin and paint fabrication, i.e. 0.0642 kWh/kg is needed.

Also the heat energy consumption is assumed to correspond to the amount consumed in the solvent-borne resin and paint fabrication, i.e. 4.44 MJ/kg is needed.

Fig. 8.5 gives an overview of the in- and output flows and Tab. 8.8 shows the ecoinvent meta data of the process.

8.5.3 Waste / Emissions

8.5.3.1 Waste heat

The heat of the electricity consumed is considered as waste heat emission to air.

8.5.3.2 Liquid / solid waste

The liquid and solid organic waste of the alkyd production process is assumed to be burned for heat generation and thus is not balanced. 1% of the input for the paint production is assumed to be disposed as waste.

8.5.3.3 Emissions to air

The VOC emissions of the alkyd production process are assumed to be burned for heat generation and thus are not inventoried. As the solvent for the paint production is water, no VOC emissions are inventoried.

8.5.3.4 Emissions to water

Eventual water emissions from cleaning etc. are not considered.

8.5.3.5 Emissions to soil

The process induces no direct soil emissions. Indirect emissions (e.g. via waste treatment) are not taken account of.

8.5.4 Transport

The standard distances and means of transport (Frischknecht et al. 2003) are assumed for the transportation of the input materials to the production plant.

8.5.5 Infrastructure

The unspecific chemical production plant is taken into account to consider the infrastructure for the process (cf. part I, Chapter 2.7).

8.6 Data quality considerations

Most data are derived from theoretical knowledge of the production process. Energy data are reported as measurement in one plant in western Europe without further information.

Alkyd resins can be produced from many different inputs. Thus neither the specific inputs nor the amounts are fixed. The inputs inventoried are described as the most commonly used.

The overall data quality is poor. The data can be used to include alkyd resins in the LCA of e.g. a building but they should not be used to compare different types of coatings.

Tab. 8.8 Meta data of the production process of alkyd paint, white, 60% in solvent, at plant

Name	alkyd paint, white, 60% in H₂O, at plant
Location	RER
Infrastructure Process	0
Unit	kg
Data Set Version	2.0
Included Processes	Transport of raw materials and production of paint. Packaging is neglected.
Amount	1
Local Name	Alkydharzlack, weiss, 60% in H ₂ O, ab Werk
Synonyms	water-reducible//wasserlöslich
General Comment to reference function	Alkyd paints can be made of many different resins. This dataset stands for one specific long oil alkyd as used in architectural paints of white colour and should not be used for other alkyds if it's contribution to the overall result is important. The data quality is not sufficient to allow for e.g. a comparative assessment of different paints.
CAS Number	
Start Date	1995
End Date	2001
Data Valid For Entire Period	1
Other Period Text	
Geography text	
Technology text	The dataset models the commonly used process for water-reducible alkyd resin production. Paint production is done by physical mixing of resin, water and pigments.
Representativeness [%]	
Production Volume	Unknown
Sampling Procedure	A "typical" water-reducible white alkyd paint is chosen and its raw material consumption is calculated. Energy data are estimated.
Extrapolations	None

General Flow information				Representation in ecoinvent							Uncertainty information			
Input	Process Name	Output	Remarks	Category	Sub category	Infrastructure	Location	Modul name in ecoinvent	Mean value	Unit	Source mean value	Type	StDv 95%	General Comment
Tall oil fatty acid	→		Soybean oil as proxy	chemicals	organics	No	RER	soya oil, at plant	1.37E-01 kg	Jones 1997	1	1.73	(4,5,5,2,3,5,3)	
Trimethylol propane	→		Pentaeritol as proxy	chemicals	organics	No	RER	penta-erythritol, at plant	8.35E-02 kg	Jones 1997	1	1.73	(4,5,5,2,3,5,3)	
Isophthalic acid	→		Phthalic anhydride as proxy	chemicals	organics	No	RER	phthalic anhydride, at plant	7.95E-02 kg	Jones 1997	1	1.73	(4,5,5,2,3,5,3)	
Trimellitic anhydrid	→			paintings	production	No	RER	white spirit, at plant	2.62E-02 kg	Jones 1997	1	1.73	(4,5,5,2,3,5,3)	
Pigment	→		reaction waste recycled as fuel --> not inventoried						8.15E-03 kg	estimate				
Auxilaries	→			chemicals	inorganics	No	RER	titanium dioxide, production mix, at plant	3.03E-01 kg	estimate, based on Jones 1997	1	1.73	(4,5,5,2,3,5,3)	
Water	→			chemicals	organics	No	GLO	chemicals organic, at plant	2.02E-02 kg	estimate, based on Jones 1997	1	1.73	(4,5,5,2,3,5,3)	
Transport rail	→			water supply	production	No	RER	water, decarbonised, at plant	3.77E-01 kg	calculated	1	1.73	(4,5,5,2,3,5,3)	
Transport lorry	→		standard distance for raw material transport	transport systems	train	No	RER	transport, freight, rail	3.90E-01 tkm	estimate	1	3.22	(5,5,5,5,5,5)	
Electricity [kWh/kg]	→		standard distance for raw material transport	transport systems	road	No	RER	transport, lorry >16t, fleet average	6.50E-02 tkm	estimate	1	3.22	(5,5,5,5,5,5)	
Heat energy [MJ/kg]	→			electricity	production mix	No	UCTE	electricity, medium voltage, production UCTE, at grid	6.43E-02 kWh	estimate, based on von Däniken & Chudacoff 1995	1	1.29	(3,4,3,3,3,1,2)	
Infrastructure (plant)	→			chemicals	organics	No	RER	heat, unspecific, in chemical plant	4.44E+00 MJ	estimate, based on von Däniken & Chudacoff 1995	1	1.29	(3,4,3,3,3,1,1)	
			waste heat	chemicals	organics	Yes	RER	chemical plant, organics	4.00E-10 unit	estimate	1	4.25	(5,5,5,5,5,5,9)	
			waste to treatment	air	unspecified			Heat, waste	2.31E-01 MJ	calculated	1	1.93	(5,5,5,2,3,5,14)	
			water-reducible alkyd paint	waste management	hazardous waste incineration	No	CH	disposal, paint remains, 0% water, to hazardous waste incineration	1.01E-02 kg	estimate	1	2.56	(5,5,5,5,5,5,6)	
				paintings	production	No	RER	alkyd paint, white, 60% in H2O, at plant	1.00E+00 kg					

Fig. 8.5 In- and Output flows of the production process of alkyd paint, white, 60% in solvent, at plant

8.7 Cumulative Results and Interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

8.8 References

- Frischknecht et al. (2007) Frischknecht R., Jungbluth N., Althaus H.-J., Doka G., Dones R., Hellweg S., Hischier R., Humbert S., Margni M., Nemecek T. and Spielmann M. (2007) Implementation of Life Cycle Impact Assessment Methods. Final report ecoinvent Data v2.0 No. 3. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.org.
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- von Däniken & Chudacoff (1995) von Däniken A. and Chudacoff M. (1995) Vergleichende ökologische Bewertung von Anstrichstoffen im Baubereich; Band 2: Daten. In: Schriftenreihe Umwelt SRU 232. Bundesamt für Umwelt Wald und Landschaft (BUWAL), Bern.

9 Allylic chloride

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9.1 Introduction

Allylic chloride ($\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$, CAS-No. 107-05-1) is at room temperature a colourless, mobile liquid that has a penetrating, pungent odour. For this inventory the functional unit is 1 kg liquid allylic chloride. The most important chemical and physical properties of allylic chloride used in this inventory are given in Tab. 9.1.

Synonyms for allylic chloride: allyl chloride, 3-chloropropene

Tab. 9.1 Chemical and physical properties of allylic chloride (according to Krähling et al. (2000))

Property	Unit	Value	Remarks
Molecular weight	g mol^{-1}	76.53	
Boiling point	°C	44.4	at normal pressure
Melting point	°C	-134	at normal pressure

9.2 Reserves and Resources of material

The production of allylic chloride is made by high temperature chlorination of propene (for more details see chapter 9.3). Therefore, all further discussion of resources can be found within the respective chapter about these two substances – here in this report for chlorine rsp. in Hischier (2007) for propene.

9.3 Use of material / product

According to Krähling et al. (2000), the most important use of allylic chloride is its function as an intermediate in the production of epichlorohydrin. Besides this, allylic chloride is also a starting material for the production of a variety of different chemicals – e.g. glycerol, esters like phthalic or carboxylic acids or allyl ethers.

From the worldwide production in the order of 850 kt in 1997, more than 90% – about 800 kt – were used for the production of epichlorohydrin, and only the remaining rest was used for other applications (Krähling et al. (2000)).

9.4 Systems characterization

In the production process for allylic chloride the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of allylic chloride is not considered to be high.

For this inventory the functional unit is 1 kg of liquid allylic chloride. As process location Europe (RER) is used. A typical process flow scheme for the production of allylic chloride is shown in Fig. 9.1.

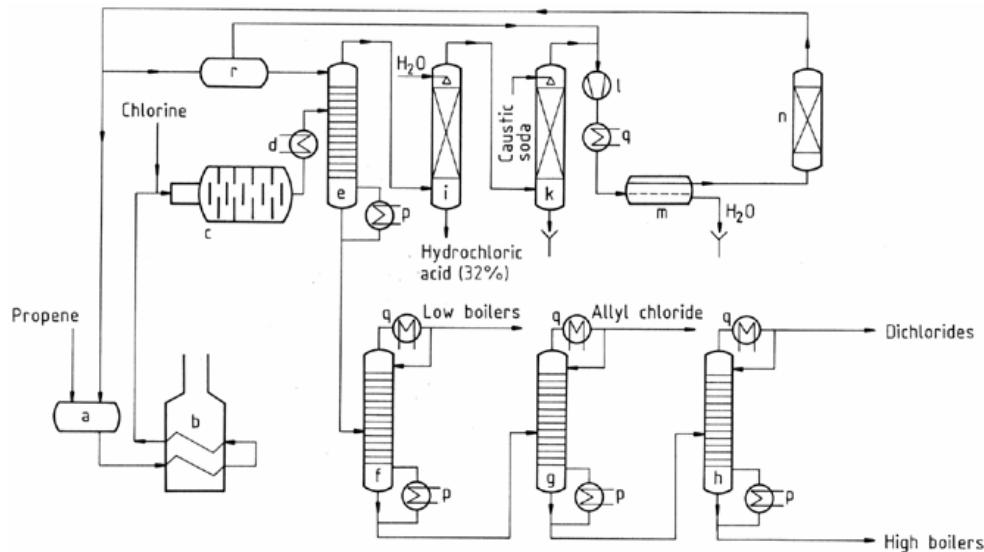


Fig. 9.1 Process chain for the production of allylic chloride (Fig.1 out of Krähling et al. (2000) – showing liquid propene storage [a], evaporator [b], the actual reactor [c], cooler [d], the different distillation steps [e] - [h], flue gas cleaning equipement [i] – [n])

According to Krähling et al. (2000), liquid propene is vaporized and preheated to 350 – 400°C. Then this gas is feed into the reactor together with gaseous chlorine. There, at about optimal conditions, chlorine reacts completely. Following to the reaction chamber are a serie of distillation steps, aiming in separating the product (allylic chloride) from unreacted substances and the in parallel synthesised by-products (mainly dichlorides like 1,2-dichloropropane and hydrogen chloride). The first step – called prefractionator – removes gaseous hydrogen chloride as well as unreacted substances (propene). In the further distillation steps the different by-products are separated from allylic chloride. The removed gaseous mixture is separated into liquid hydrogen chloride (by adding water) and propene. The latter one is washed with sodium hydroxide and then re-liquified and goes back to the beginning of the process scheme.

9.5 Allylic chloride, at plant (Location: RER)

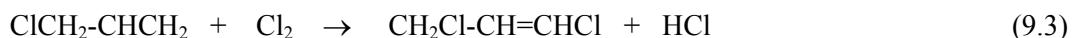
9.5.1 Process

This dataset includes a rough estimation of the production process for allylic chloride. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The chlorination reaction for the production of allylic chloride can be formulated as follows:



As already mentioned above, besides the main reaction several other reactions lead to the production of different by-products. The two most important reactions are leading to the production of 1,2-dichloropropane resp. cis-/trans-1,3-dichloropropene:



Further reactions of already chlorinated propane with additional chlorine – according to eq.1.3 – can lead to even higher chlorinated substances.

The yield of the different reactions – all of them are exothermic – is strongly depending from the actual temperature in the reaction chamber as well as the ratio of propene and chlorine feed in. As a general rule it can be said that the reaction temperature has to be at least 250 - 300°C (as below the production of 1,2-dichloropropane is the dominating reaction). Additionally, the more propene the less by-products are formed with the inconvenient that the cost of processing propene rises accordingly.

For this study, a propene : chlorine ratio of 3 is assumed, with a preheating temperature for the propene to 300°C (Krähling et al. (2000)). The reaction time is quite short – e.g. chlorine reacts completely at such temperatures within a few seconds. Therefore, a yield of 99% is assumed for chlorine. Concerning the propene input, an amount equal 101% of the stoichiometric amount is used, as the excess propene goes back within the process (closed circle) – 101% as losses (see chapter 9.5.3) are also taken into account here.

After removing the excess propene together with the produced hydrogen chloride, Krähling et al. (2000) indicates the distribution to the different products as 80% allylic chloride, 3% other monochlorides, 16% dichlorides (e.g. 1,2-dichloropropane) and 1% trichlorides. Therefore it is assumed in this study a distribution of the dichlorides to 50% 1,2-dichloropropane and 50% cis/trans-1,3-dichloro-1-propene. All these further substances are accounted for as by-products and not as co-product due to the fact that the process is regulated accordingly to an optimum output of allylic chloride.

9.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the waste water treatment. Fossil fuel is needed to generate the desired heat for the preheating and the distillation of the product. There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the allylic chloride production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was used. A summary of the values used is given in Tab. 9.2.

Raw materials and Chemicals

According to the above listed distribution of the different by-products, the production of 1 kg allylic chloride produces also 37.5g of further monochlorides, 200g of dichlorides and 12.5g of trichlorides. For a production of all these products, the following stoichiometric inputs are needed (yield 100%):

- propene, CH₂=CH-CH₃: 648.669 g (15.445 mol)
- chlorine, Cl₂: 1172.061 g (16.517 mol)

For the production a yield of 99% for chlorine was used according to the implications above. For propene, according to the text above, 101% of the stoichiometric amount goes into the process. Therefore 655.155 g propene and 1183.900 g chlorine are considered as raw materials in this inventory. A summary of the values used is given in Tab. 9.2.

Besides chlorine and propene, the cleaning and feeding back of excess propene needs sodium hydroxide as a cleaning agent. Assuming that 0.5% of the produced hydrogen chloride remains in the excess

propene, a stoichiometric amount of 3.155 g NaOH is needed. For this study it is assumed that NaOH is added with an excess of 25%, leading to an input amount of 3.944 g NaOH.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the allylic chloride production.

For the process water amount, due to a lack of data, an amount of 25% of the cooling water amount is assumed here – leading to an input of 6 kg water per kg allylic chloride.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg allylic chloride was included.

9.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg allylic chloride is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of allylic chloride. As approximation the air emissions occurring from the purge vent, the distillation vent and fugitive emission sources were estimated to 0.2% of the raw material input as well as 0.5% of the produced hydrogen chloride.

This assumption leads to air emissions of 1.297 g propene, 2.368 g chlorine and 2.850 g hydrogen chloride.

Emissions to water

The remaining amount of unreacted chlorine was assumed to leave the production process with the waste water. From propene an amount of 0.8% is assumed to leave in the waste water (while the excess amount is recovered). Further emissions to water are hydrogen chloride (assuming that again 0.5% of HCl are emitted) and the total amount of sodium hydroxide input. All these assumptions lead to a pollution of the waste water with 9.565 g chlorine, 2.850 g hydrogen chloride, 3.944 g of sodium hydroxide and 5.189 g propene.

Further it was assumed that this waste water is treated in an internal waste water plant. The removal efficiency for propene was assumed with 90% leading to emissions of 0.519 g propene per kg product in the treated water. The carbon contained in the removed propene was accounted as CO₂ emissions to air

(14.678 g CO₂ per kg product). NaOH, HCl and Cl₂ are supposed to leave the plant as the respective ions - i.e. as 2.268 g Na⁺ and 12.415 g Cl⁻. The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of propene in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 9.2.

Solid wastes

Solid wastes occurring during the production of allylic chloride were neglected in this inventory.

Tab. 9.2 Energy demand, Resource demand and emissions for the production of allylic chloride.

[per kg allyl chloride]			Remark
INPUTS			
propene	kg	0.655	stoichiometric calc., 101%
chlorine	kg	1.184	stoichiometric calc., 99% yield
sodium hydroxide	kg	0.004	stoichiometric calc., 25% excess
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m ³	2.40E-02	estimation
Water, unspecified	m ³	1.20E-02	estimation
transport by train	tkm	1.11E+00	standard distances
transport by lorry, 32t	tkm	1.84E-01	standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
propene, to air	kg	1.30E-03	estimated as 0.2% of input
chlorine, to air	kg	2.37E-03	estimated as 0.2% of input
hydrogen chloride, to air	kg	2.85E-03	estimated as 0.5% of produced amount
carbon dioxide, fossil, to air	kg	1.47E-02	from waste water treatment
propene, to water	kg	5.19E-04	calculated from mass balance
chloride ions, to water	kg	1.24E-02	calculated from mass balance
sodium ions, to water	kg	2.27E-03	calculated from mass balance
COD, BOD	kg	1.70E-03	calculated from water emissions
TOC, DOC	kg	4.44E-04	calculated from water emissions

9.6 Data quality considerations

Tab. 9.3 shows the data quality indicators for the inventory of allylic chloride production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the allylic chloride production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data.

Additionally, the most important fields of the ecospold meta information from those datasets are listed in 9.9.

Tab. 9.3 Input / Output and uncertainty for the process “allylic chloride, at plant (RER)”

Explanation	Name	Location	Unit	allylic chloride, at plant		UncertaintyType standardDeviation95%	GeneralComment		
				Location					
				Infrastructure	Process				
Resource Input from Technosphere	Water, cooling, unspecified natural origin	m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant			
	Water, unspecified natural origin	m3	1.20E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant			
	propylene, at plant	RER	kg	6.55E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	chlorine, liquid, production mix, at plant	RER	kg	1.18E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	4.00E-03	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation		
	transport, freight, rail	RER	tkm	1.11E+00	1	2.09	(4,5,na,na,na,na); standard distances		
	transport, lorry 32t	RER	tkm	1.84E-01	1	2.09	(4,5,na,na,na,na); standard distances		
Output Air emission Water emission	allylic chloride, at plant	RER	kg	1					
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input		
	Carbon dioxide, fossil		kg	1.47E-02	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Propene		kg	1.30E-03	1	2.32	(5,5,na,na,na,5); estimation		
	Chlorine		kg	2.37E-03	1	2.32	(5,5,na,na,na,5); estimation		
	Hydrogen chloride		kg	2.85E-03	1	2.32	(5,5,na,na,na,5); estimation		
	BOD ₅ , Biological Oxygen Demand		kg	1.70E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	COD, Chemical Oxygen Demand		kg	1.70E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	DOC, Dissolved Organic Carbon		kg	4.44E-04	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	TOC, Total Organic Carbon		kg	4.44E-04	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Propene		kg	5.19E-04	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Chloride		kg	1.24E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Sodium, ion		kg	2.27E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		

9.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

9.8 Conclusions

The inventory for allylic chloride is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if allylic chloride is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

9.9 EcoSpold Meta Information

ReferenceFunction	Name	allylic chloride, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Allylchlorid, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid allylic chloride. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	107-05-1
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from propene and chlorine with a process yield of 99% for chlorine (propene is added as 101% of stoichiometric amount). Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

9.10 References

- Frischknecht et al. (2007) Frischknecht R., Althaus H.-J., Doka G., Dones R., Hischier R., Hellweg S., Jungbluth N., Kellenberger D., Nemecek T., Rebitzer G. and Spielmann M. (2007) Overview and Methodology. Final report ecoinvent Data v2.0 No. 1. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.
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http://www.mrw.interscience.wiley.com/ueic/ull_search_fs.html.

10 Aluminium fluoride and cryolite

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10.1 Introduction

Aluminium fluoride (AlF_3 , CAS-No. 7784-18-1) as well as cryolite ($\text{AlF}_3 \cdot 3\text{NaF}$, CAS-No. 15096-52-3) are almost exclusively used within the aluminium production. According to Mollard (2000), more than 95% of the two substances are used in the baths for electrolytic aluminium production.

Aluminium fluoride with a molecular weight of 83.92 g/mol is at room temperature a white solid. Under atmospheric pressure conditions, AlF_3 has no boiling and melting point – instead it has a sublimation point at around 1275°C.

Cryolite is the most important fluoroaluminate used in industry. Like the simple aluminium fluoride, it is a solid – having a molecular weight of 209.94 g/mol – with monoclinic crystalline structure. The melting point of this substance is about 1010°C.

10.2 Reserves and Resources of material

The production of aluminium fluoride as well as cryolite is made out of aluminium oxides and hydrofluoric acid (for more details see chapter 10.4). Therefore, all further discussion of resources can be found within the respective chapter about these two substances – in Jungbluth (2007) for hydrofluoric acid rsp. in Classen et al. (2007) for aluminium oxide.

10.3 Use of material / product

As already mentioned in the introduction, almost all of these two substances is used in the electrolysis cells for the production of aluminium (Mollard (2000)). From aluminium fluoride up to 15-20 kg/t aluminium are used. Cryolite – although it is the principal constituent of the electrolysis bath for the aluminium production – is used in much less quantities (around 4-10 kg/t aluminium).

Other uses of the two substances – although they are of much less importance – are the use in special glasses for optical purposes, in ceramics and as protector of baths for the refining of light metals. Cryolite is furthermore also used as filler in resins and grinding wheels.

The worldwide production of aluminium fluoride was in 1990 in the order of 700 kt – for cryolite no similar numbers were available.

10.4 Systems characterization

10.4.1 Aluminium fluoride

In the production process for aluminium fluoride the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of aluminium fluoride is not considered to be high.

For this inventory the functional unit is 1 kg of solid aluminium fluoride. As process location Europe (RER) is used. For the production two different processes are possible – the hydrofluoric acid process and the fluosilicic acid process. As the first one is only very few used – in this study it is assumed that aluminium fluoride is produced only by the fluosilicic acid process. A typical process flow scheme for the production of aluminium fluoride according to this process is shown in Fig. 10.1.

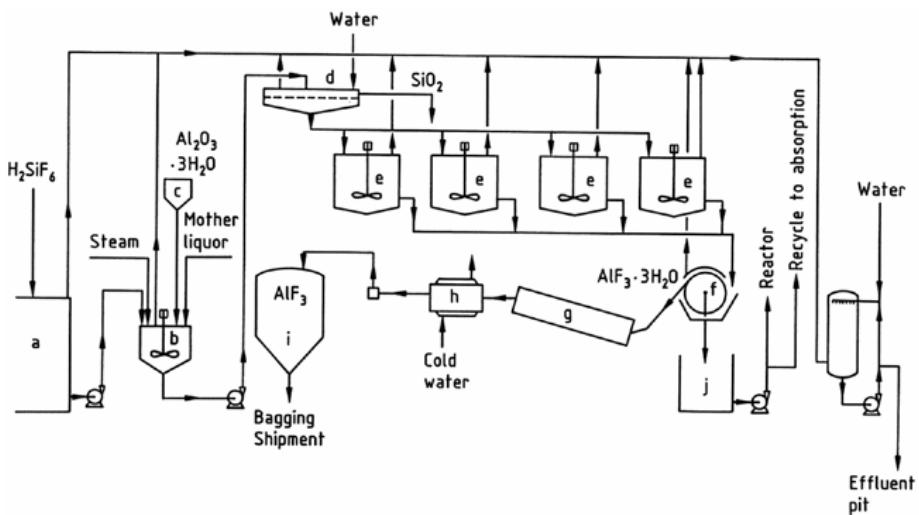


Fig. 10.1 Process chain for the production of aluminium fluoride (Fig.5 out of Mollard (2000) – showing H_2SiF_6 storage tank [a], reactor [b], alumina hopper [c], silica filter [d], crystallizer [e], trihydrate filter [f], drier [g], cooler [h], finished product storage hopper [i] and weak mother liquor storage tank [j])

According to Mollard (2000), alumina trihydrate is dissolved either batchwise or continuous in fluosilicic acid, preheated to 60°C. After 20 minutes the reaction is complete and the by-product silica is filtered off. The remaining AlF_3 solution is put into stirred tanks for 5 to 8 hours where the crystallization takes place.

10.4.2 Cryolite

In the production process for cryolite the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of cryolite is not considered to be high.

For this inventory the functional unit is 1 kg of solid cryolite. As process location Europe (RER) is used. For its production, like for aluminium fluoride, two different processes are possible too – the hydrofluoric acid as well as the fluosilicic acid technique. Mollard (2000) doesn't contain any information concerning the split between the different techniques – therefore, in this study it is assumed that all cryolite is produced by the hydrofluoric acid process. There, in a first reaction alumina trihydrate is dissolved batchwise in hydrofluoric acid during an hour at 70°C. In a second step, cryolite is precipitated by adding sodium hydroxide, sodium carbonate or sodium chloride. In this study, an input of sodium hydroxide is used.

10.5 Aluminium fluoride, at plant (Location: RER)

10.5.1 Process

This dataset includes a rough estimation of the production process for aluminium fluoride. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

According to chapter 10.4.1, all aluminium fluoride in this study is produced by the fluosilicic acid process. The overall reaction can be summarized as:



10.5.2 Resources

Energy

There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the aluminium fluoride production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 10.1.

Raw materials

According to the above shown reaction equations - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of aluminium fluoride:

- fluosilicic acid, H_2SiF_6 : 587.883 g (5.954 mol)
- Alumina trihydrate, $\text{Al}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$: 928.554 g (5.954 mol)

For the production a yield of 98% for the overall reaction is used. Furthermore it is assumed that fluosilicic acid is 100% from the recovery of fluorine in the phosphate industry – and therefore enters into this dataset here without any environmental load (according to the methodology of the study) and is therefore not shown as input. Thus 947.505 g alumina trihydrate is considered as the only raw material input in this inventory. As there is only anhydrous alumina available within the ecoinvent database, this input here is approximated by the same molar amount of alumina – i.e. 619.438 g. The produced water is part of the waste water leaving the production. A summary of the values used is given in Tab. 10.1.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the aluminium fluoride production.

For the process water amount, due to a lack of data, an amount of 50% of the cooling water amount is assumed here – leading to an input of 12 kg water per kg aluminium fluoride.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg cryolite was included.

10.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg aluminium fluoride is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of aluminium fluoride. As approximation the air emissions were estimated to 0.2% of the raw material input (without alumina). This assumption leads to air emissions of 1.751 g fluosilicic acid.

Emissions to water

From the remaining amount of unreacted fluosilicic acid it is assumed that 80% are staying within the production site in the weak mother liquor and only the remaining 20% of the unreacted substance are to leave the production process with the waste water, leading to a pollution of the waste water with 3.151 g fluosilicic acid. It is assumed that the waste water treatment will not recover this substance and thus, 3.151 g fluosilicic acid are leaving in the waste water.

Solid wastes

Solid wastes occurring during the production of aluminium fluoride were neglected in this inventory.

Tab. 10.1 Energy demand, Resource demand and emissions for the production of aluminium fluoride.

[per kg aluminium fluoride]			Remark
INPUTS			
fluosilicic acid	kg	0.600	not shown in dataset
alumina trihydrate	kg	9.48E-01	shown as 0.619 kg alumina in dataset
Water, cooling, unspecified	m3	2.40E-02	estimation
Water, process, unspecified	m3	1.20E-02	estimation
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
transport by train	tkm	7.31E-01	calculated with standard distances
transport by lorry	tkm	1.22E-01	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
fluosilicic acid, to air	kg	1.75E-03	estimated as 0.2% of input
fluosilicic acid, to water	kg	3.15E-03	estimated, assuming 20% of unreacted substance in waste water

10.5.4 Data quality considerations

Tab. 10.2 shows the data quality indicators for the inventory of aluminium fluoride production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the aluminium fluoride production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data.

Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 10.9.

Tab. 10.2 Input / Output and uncertainty for the process “aluminium fluoride, at plant (RER)”

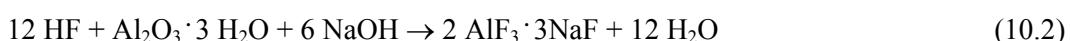
Explanation	Name	Location	Unit	aluminium fluoride, at plant		uncertaintyType	standardDeviation95%	GeneralComment
				RER	o			
				kg	kg			
Resources	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	Water, unspecified natural origin		m3	1.20E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	aluminium oxide, at plant	RER	kg	6.19E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation	
	transport, freight, rail	RER	tkm	7.31E-01	1	2.09	(4,5,na,na,na,na); standard distances	
	transport, lorry 32t	RER	tkm	1.22E-01	1	2.09	(4,5,na,na,na,na); standard distances	
Output	aluminium fluoride, at plant	RER	kg	1				
Air emission	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input	
	Fluosilicic acid		kg	1.75E-03	1	2.32	(5,5,na,na,na,5); estimation	
water emission	Fluosilicic acid		kg	3.15E-03	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	

10.6 Cryolite, at plant (Location: RER)

10.6.1 Process

This dataset includes a rough estimation of the production process for cryolite. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

According to chapter 10.4.2, all cryolite is produced by the hydrofluoric acid process, using sodium hydroxide for the precipitation. The overall reaction can be summarized as:



10.6.2 Resources

Energy

There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the cryolite production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 10.3.

Raw materials

According to the above shown reaction equations - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of cryolite:

- Hydrofluoric acid, HF: 571.878 g (28.580 mol)
- Alumina trihydrate, $\text{Al}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$: 371.440 g (2.382 mol)
- Sodium hydroxide, NaOH: 571.592 g (14.290 mol)

For the production a yield of 98% for the overall reaction is used. Therefore 583.549 g hydrofluoric acid, 379.020 g alumina trihydrate and 583.257 g sodium hydroxide are considered as raw materials in this inventory. As there is only anhydrous alumina available within the ecoinvent database, this input here is approximated by the same molar amount of alumina – i.e. 247.787 g. The produced water is part of the waste water leaving the production. A summary of the values used is given in Tab. 10.3.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the cryolite production.

For the process water amount, due to a lack of data, an amount of 25% of the cooling water amount is assumed here – leading to an input of 6 kg water per kg cryolite.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg cryolite was included.

10.6.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg aluminium fluoride is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of aluminium fluoride. As approximation the air emissions occurring from the purge vent, the distillation vent and fugitive emission sources were estimated to 0.2% of the HF input.

This assumption leads to air emissions of 1.167 g hydrofluoric acid.

Emissions to water

The remaining amount of un-reacted hydrofluoric acid as well as sodium hydroxide was assumed to leave the production process with the waste water, leading to a pollution of the waste water with 10.504 g hydrofluoric acid and 10.499 g sodium hydroxide. As both substances are dissolved in water, a waste water treatment plant is not assumed here – thus, the process releases 9.979 g F⁻ and 6.037 g sodium ions in the leaving water.

Solid wastes

Solid wastes occurring during the production of aluminium fluoride were neglected in this inventory.

Tab. 10.3 Energy demand, Resource demand and emissions for the production of cryolite

[per kg cryolite]	Remark		
INPUTS			
hydrofluoric acid	kg	0.584	stoichiometric calc., 98% yield
alumina trihydrate	kg	0.379	shown as 0.248 kg alumina in dataset
sodium hydroxide	kg	5.83E-01	stoichiometric calc., 98% yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m ³	2.40E-02	estimation
Water, process, unspecified	m ³	1.20E-02	estimation
transport by train	tkm	8.49E-01	calculated with standard distances
transport by lorry	tkm	1.41E-01	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
hydrofluoric acid, to air	kg	1.17E-03	estimated as 0.2% of input
fluoride, to water	kg	9.98E-03	calculated from mass balance
sodium ions, to water	kg	6.04E-03	calculated from mass balance

10.6.4 Data quality considerations

Tab. 10.4 shows the data quality indicators for the inventory of cryolite production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the cryolite production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 10.9.

Tab. 10.4 Input / Output and uncertainty for the process “cryolite, at plant (RER)”

Explanation	Name	Location	Unit	cryolite, at plant		GeneralComment
				RER	0 kg	
				uncertaintyType	standardDeviation95%	
Resource Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88 (5.5,1,1,4,5); estimated with data from a large chem. plant
	Water, unspecified natural origin		m3	1.20E-02	1	1.88 (5.5,1,1,4,5); estimated with data from a large chem. plant
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	5.83E-01	1	1.21 (4,na,na,na,na,na); estimation based on process yield 90-99.8%
	hydrogen fluoride, at plant	GLO	kg	5.84E-01	1	1.21 (4,na,na,na,na,na); estimation based on process yield 90-99.8%
	aluminiun oxide, at plant	RER	kg	2.48E-01	1	1.21 (4,na,na,na,na,na); estimation based on process yield 90-99.8%
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88 (5.5,1,1,4,5); estimated with data from a large chem. plant
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88 (5.5,1,1,4,5); estimated with data from a large chem. plant
	chemical plant, organics	RER	unit	4.00E-10	1	3.77 (4,5,1,3,5,4); estimation
	transport, freight, rail	RER	tkm	8.49E-01	1	2.09 (4,5,na,na,na,na); standard distances
	transport, lorry 32t	RER	tkm	1.41E-01	1	2.09 (4,5,na,na,na,na); standard distances
Output Air emission	cryolite, at plant	RER	kg	1		
	Heat, waste		MJ	1.20E+00	1	1.88 (5,5,1,1,4,5); calculated from electricity input
	Hydrogen fluoride		kg	1.17E-03	1	2.32 (5,na,na,na,5); estimation
	Sodium, ion		kg	6.04E-03	1	2.11 (5,5,na,na,4,5); estimated from mass balance and WWTP effic.
Water emission	Fluoride		kg	9.98E-03	1	2.11 (5,na,na,4,5); estimated from mass balance and WWTP effic.

10.7 Cumulative results and interpretation

Results of the cumulative inventory for both substances can be downloaded from the database.

10.8 Conclusions

The inventories for aluminium fluoride and cryolite are based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if these substances are used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of these materials with other, alternative products.

10.9 Ecospold Meta Information

ReferenceFunction	Name	aluminium fluoride, at plant	cryolite, at plant
Geography	Location	RER	RER
ReferenceFunction	InfrastructureProcess	0	0
ReferenceFunction	Unit	kg	kg
	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1	1
ReferenceFunction	LocalName	Aluminiumfluorid, ab	Kryolith, ab Werk
ReferenceFunction	Synonyms		
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of solid aluminium fluoride. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.	The functional unit represent 1 kg of solid cryolite. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	7784-18-1	15096-52-3
TimePeriod	StartDate	2000	2000
TimePeriod	EndDate	2000	2000
TimePeriod	DataValidForEntirePeriod	1	1
TimePeriod	OtherPeriodText	date of published literature	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production by the fluosilicic acid process. Alumina trihydrate is dissolved in fluosilicic acid and then crystallization takes place in a stirred tank. The overall process yield is of 98%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant	Production by the hydrofluoric acid technique. In a first step, alumina trihydrate is leached by hydrofluoric acid - in the second step cryolite is precipitated by adding sodium hydroxide. The overall process yield is of 98%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of HF input) and water were estimated using mass balance.
Representativeness	Percent		
Representativeness	ProductionVolume		
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations		
Representativeness	UncertaintyAdjustments	none	

10.10 References

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11 Ammonia

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 Review: Heiko Kunst, TU Berlin

11.1 Introduction

Ammonia (NH_3 , CAS-No. 7664-41-7) is a colourless gas with a penetrating, pungent suffocating odour detectable at 17 ppm. When under pressure it is a liquid. It is hygroscopic and soluble in water (89.9 g/L at 0°C). The most important chemical and physical properties are summarised in Tab. 11.1.

Synonyms for ammonia: anhydrous ammonia, liquid ammonia.

Tab. 11.1 Chemical and physical properties of ammonia (Chemfinder 2002).

Property	Value	Unit	Property	Value	Unit
Molecular weight	17.0304	g mol^{-1}	Melting point	-77.73	°C
Density (at 20°C)	0.6818	g cm^{-3}	Boiling point	-33.34	°C

The following descriptions of reserves and resources, production technology and the use of nitric acid are summarised from EFMA (2000) and Bakemeier *et al.* (1985).

11.2 Reserves and Resources

Ammonia is produced basically from air and gas according the steam reforming process. With the partial oxidation process the basic raw materials are liquid nitrogen on one side and on the other, residual oils or coal, highly viscous hydrocarbons or plastic wastes. The resources available as well as the reserves are in the case of the steam reforming process depend only on the reserves of natural gas. If considering the partial oxidation, the production depends on other manufacturing processes with their own specific dynamics.

Based on the known resources of fossil fuel, it is likely that natural gas will predominate as feedstock for the production of ammonia for the next 50 years at least. In a long-term perspective, 50 to 100 years from now, coal may take over as feedstock, based on world reserves and consumption rate.

11.3 Production Technologies and Use

11.3.1 Production technologies for ammonia

According to EFMA (2000), two main types of production processes for ammonia synthesis gas are currently in operation in Europe:

- Steam reforming of natural gas or other light hydrocarbons (natural gas liquids, liquefied petroleum gas, naphtha) and
- Partial oxidation of heavy fuel oil or vacuum residue

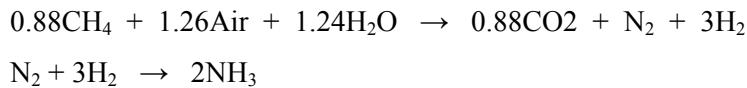
Coal gasification and water electrolysis are no longer in use in the European ammonia industry.

The ammonia synthesis process is principally independent of the type of synthesis gas production process, but synthesis gas quality influences the loop design and operation conditions.

Conventional Steam Reforming

About 85% of world ammonia production is based on steam reforming concepts. A block diagram of the conventional steam reforming process is shown in Fig. 11.1. (In some cases, a separate auxiliary boiler is required)

The theoretical process conversions, based on methane feedstock, are given in the following approximate formulae:



Various feedstocks are available, but most of the ammonia plants use natural gas to supply hydrogen. The use of alternate feedstocks, such as naphtha, fuel oil and coal has been evaluated, but natural gas is the most convenient.

Desulphurization of the feedstock is the first step in the ammonia manufacturing process. The sulphur concentration is reduced to below 0.1 ppm to avoid adverse effects on the reformer catalysts. Desulphurization is typically performed using a cobalt molybdenum catalyst and then a pelletised zinc oxide bed. Zinc sulphide remains in the adsorption bed. The hydrogen for the reaction is usually recycled from the synthesis section.

The gas from the desulphuriser is mixed with process steam coming from an extraction turbine, and the steam/gas mixture is then heated further in the convection section before entering the primary reformer. This consists of a large number of high-nickel chromium alloy tubes filled with nickel-containing reforming catalyst. In the primary reformer the gas yields hydrogen and carbon monoxide, under high temperature and pressure. Since this reaction is highly endothermic, additional heat is required. This is achieved by burning natural gas or other gaseous fuel in burners of a radiant box containing the tubes. After supplying the necessary high level heat to the reforming process, this gas has a surplus of heat content. (Only about 50-60% of the fuel's heat value is used in the process itself). This surplus is recovered for its reuse in the production process.

Only 30 to 40% of the hydrocarbon feed are reformed in the primary reformer because of the chemical equilibrium at the actual operating conditions. The temperature must be raised to increase the conversion. This is done in the secondary reformer by internal combustion of part of the gas with the process air, which also provides the nitrogen for the final synthesis gas.

After being cooled, the gas enters a two stage converter called shift section, where the carbon monoxide (CO) in the process gas undergoes a conversion to carbon dioxide (CO₂). The removal of the CO is important for the efficiency of the process. In the high temperature shift converter the CO present in the gas reacts with steam, thereby producing CO₂ and hydrogen. The gas is cooled and enters the low temperature shift converter, where additional CO is removed. The converters use iron oxide/chromium oxide- and copper oxide/zinc oxide-based catalysts. At this point, the process gas contains mainly H₂, N₂, CO₂ and the excess process steam. The gas is cooled and most of the excess steam is condensed before it enters the CO₂ removal system. Minor amounts of amines, formic acid and acetic acid could be present in the condensate. All these components are stripped from the condensate and/or recycled if using BAT techniques. The heat released during cooling/condensation is further used in the production process.

Since CO₂ adversely affects the catalyst used in ammonia synthesis it is removed from the gas stream through scrubbing with monoethanolamine, activated diethanolamine or hot potassium carbonate solution (chemical absorption process). Instead of the mentioned process, physical absorption can also be used. Physical solvents are glycol dimethylethers (selenexol), propylene carbonate and others. The liquor is regenerated using steam stripping.

The next step is methanation. The small amounts of CO and CO₂ remaining in the gas are poisonous for the ammonia synthesis catalyst and must be removed by conversion to methane (CH₄) in the methanator. Methane is formed by a reaction between H₂ and trace amounts of CO and CO₂ present in

the gas, with the reaction occurring in the presence of a nickel catalyst. The purified gas is comprised at this point of H₂, nitrogen and small quantities of argon, CH₄ and helium. This gas is then compressed and routed to the synthesis operation.

The compressed gas enters the ammonia converter, where ammonia is synthesised by reacting H₂ and N₂ in the presence of an iron catalyst. In order to attain the necessary high pressures, small plants use reciprocating compressors, while larger plants implement centrifugal machines for gas compression. Modern ammonia plants use centrifugal compressors for synthesis gas compression, usually driven by steam turbines, with the steam being produced in the ammonia plant. The refrigeration compressor, needed for condensation of product ammonia, is also usually driven by a steam turbine.

Only 10 to 20 % of the gas is converted to ammonia per pass in the converter due to unfavourable equilibrium conditions. The ammonia that is formed is separated from the recycle gas by cooling/condensation, and the reacted gas is substituted by the fresh make-up synthesis gas, thus maintaining the loop pressure. In addition, extensive heat exchange is required due to the exothermic reaction and the large temperature range in the loop.

Conventional reforming with methanation as the final purification step produces a synthesis gas containing inerts (CH₄ and argon) in quantities that does not dissolve in the condensed ammonia. The major part of these inerts is removed by taking out a purge stream from the loop. The purge gas is scrubbed with water to remove ammonia before being used as fuel or before being sent for hydrogen recovery.

In most ammonia plants and in order to achieve an efficient ammonia condensation, vaporising ammonia is used as a refrigerant (instead of water or air) to achieve sufficiently low ammonia concentrations in the gas recycled to the converter. The ammonia vapours are liquefied after recompression in the refrigeration compressor.

Production of Carbon Dioxide

Carbon Dioxide is a by-product generated according to a stoichiometric conversion and may be recovered for down stream uses.

Other steam reforming processes

The **excess air steam reforming process** is similar to the conventional, but just more efficient. The features diverging from conventional steam reforming are: decreased firing in the primary reformer, increased process air flow to the secondary reforming, cryogenic final purification and lower synthesis gas inert level.

The **heat exchange autothermal reforming** was 1999 mostly at the pilot stage, with only two manufacturing plants operating such process. Instead of using the heat of the two reformer outlet gas just to raise steam (what is wasteful from a thermodynamic point of view), it is recycled to the process itself. This is achieved by using this heat in a newly developed primary reformer thus eliminating the fired furnace.

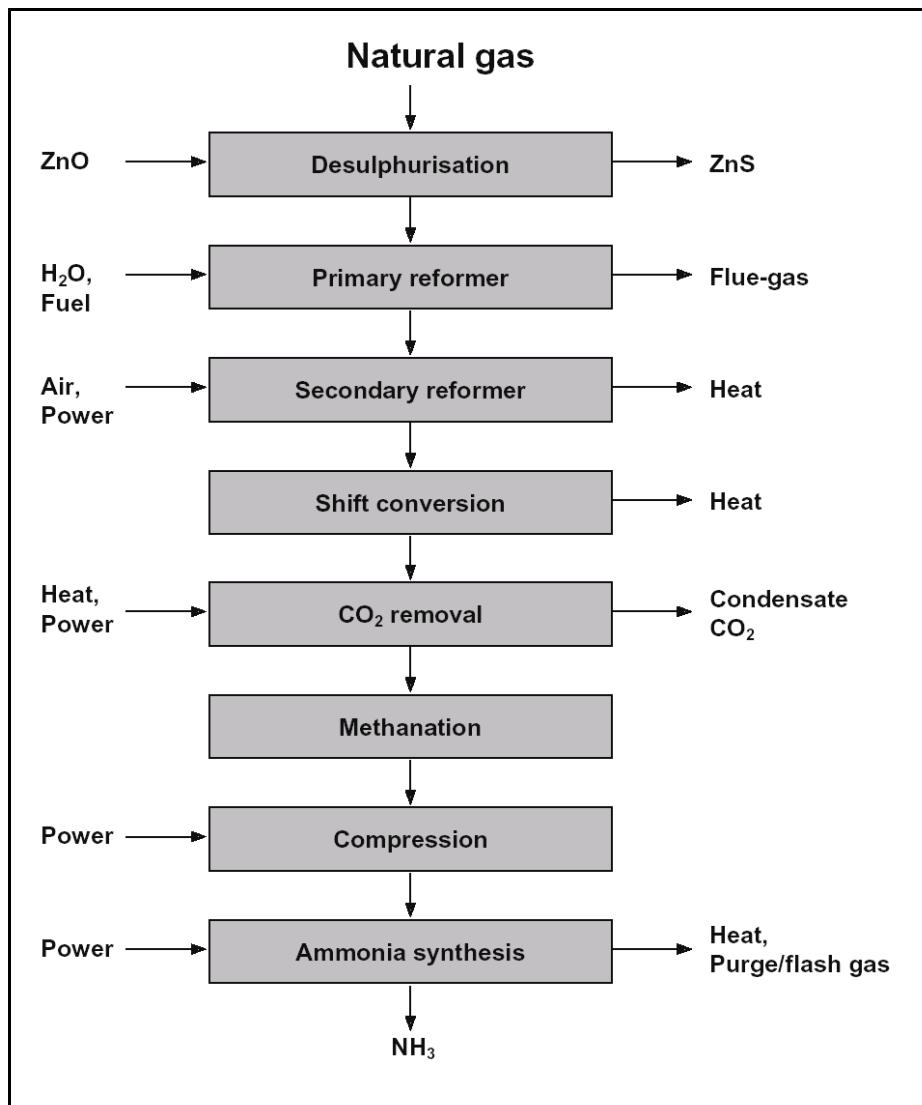


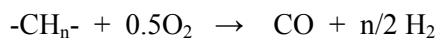
Fig. 11.1 Ammonia production with conventional steam reforming. (Taken from Fig. 1, EFMA (2000))

11.3.2 Partial oxidation

The partial oxidation process is used for the gasification of heavy feedstocks such as residual oils and coal. Extremely viscous hydrocarbons and plastic wastes may also be used as fractions of the feed. Thus, the partial oxidation process offers an alternative for future utilisation of such wastes. A block diagram of the partial oxidation process is shown in Fig. 11.2

An air separation unit is required for the production of oxygen for the partial oxidation step. The nitrogen is added in the liquid nitrogen wash to remove impurities from the synthesis gas and to get the required hydrogen/nitrogen ratio in the synthesis gas.

The partial oxidation gasification is a non-catalytic process taking place at high pressure and temperature. The simplified reaction pattern is:



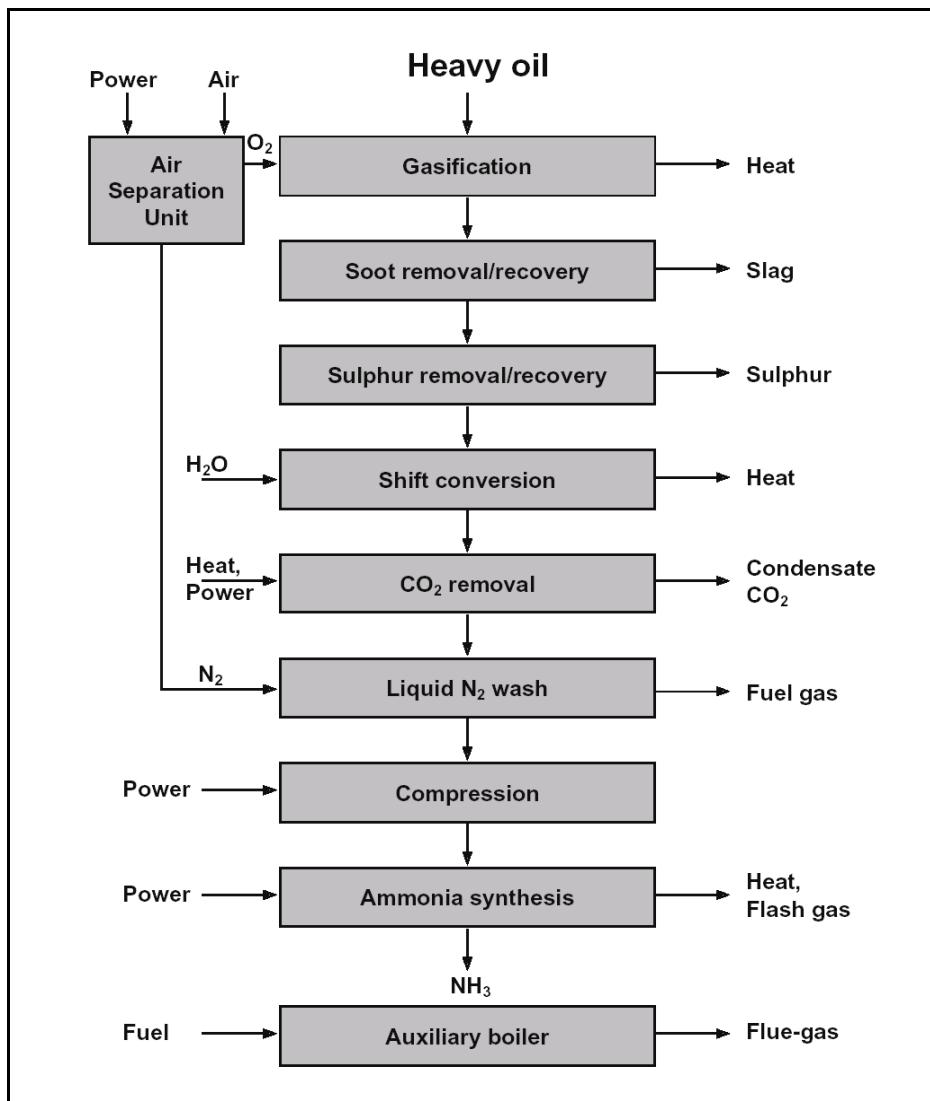


Fig. 11.2 Ammonia production with partial oxidation. (Taken from Fig. 2, EFMA (2000))

Carbon dioxide, methane and some soot are formed in addition. The sulphur compounds in the feed are converted to hydrogen sulphide. Mineral compounds in the feed are transformed into specific ashes. The process gas is freed from solids by water scrubbing after waste heat recovery and the soot is recycled to the feed. The ash compounds are drained with the process condensate and/or together with a part of the soot. The heavy metals are recovered. The hydrogen sulphide in the process gas is separated in a selective absorption step and reprocessed to elementary sulphur in a Claus unit.

The shift conversion usually has two high temperature shift catalyst beds with intermediate cooling. Steam for the shift conversion is supplied partially by a cooler-saturator system and partially by steam injection.

CO_2 is removed by using an absorption agent that might be the same as that in the sulphur removal step. Residual traces of absorption agent and CO_2 are then removed from the process gas, before final purification by a liquid nitrogen wash. In this unit practically all the impurities are removed and nitrogen is added to give the stoichiometric hydrogen to nitrogen ratio.

The ammonia synthesis is quite similar to that used in steam reforming plants, but simpler and more efficient, due to the high purity of synthesis gas from liquid nitrogen wash units and the synthesis loop not requiring a purge.

No major improvements are to be expected concerning process efficiency and plant investment costs. However, partial oxidation will continue to be interesting in the future, due to its feedstock flexibility. The separation and disposal of the soot and especially the ashes are necessary to adapt to deteriorating residue qualities or alternative raw material sources.

Production of Carbon Dioxide

Carbon Dioxide is a by-product generated according to a stoichiometric conversion and may be recovered for down stream uses.

11.3.3 Product storage and loading

The ammonia product is stored in large atmospheric tanks at a temperature of -28 °C or in large spheres maintained at pressures up to 20 atm at ambient temperatures.

11.3.4 Use

Based on value, synthetic ammonia is one of the most important chemical products worldwide.

The most important use for ammonia is as a supply of vital agricultural nitrogen for crops. It is either applied as a fertiliser directly or it is used as a feedstock in the manufacture of urea, ammonium nitrate or nitric acid.

The industrial use of ammonia as a nitrogen source has consumed an increasingly greater share of total ammonia production, amounting now to about 20% of world output. Virtually all nitrogen used in the chemical industry enters the process as ammonia. The major uses of industrial ammonia-nitrogen , in part after conversion into nitric acid, are the manufacture of plastics and fibres. Other important applications are the manufacture of explosives, hydrazine, amines, amides, nitriles, and other organic nitrogen compounds serving as intermediates for dyes and pharmaceuticals. The most important products manufactured from ammonia are nitric acid, urea, sodium cyanide and sodium carbonate.

Ammonia is used in the area of environmental protection to remove SO₂ and NO_x from steam boiler flue gases. The resulting ammonium sulphate (and sometimes ammonium nitrate) is marketed as a fertiliser product. Liquid ammonia has a considerable importance as a solvent. Ammonia is also used in the nitriding of steel. It is also still used as a refrigerant in industrial and commercial refrigeration and air-conditioning installations.

Ammonia is an inexpensive and easily managed starting material for manufacturing protective gas mixtures for chemical products and for metal-working processes. It is also used for manufacturing hydrogen and is even proposed for use in energy-related applications

11.4 System Characterisation

This report refers to four modules in Ecoinvent database. The first refers to **1 kg liquid ammonia, steam reforming, at plant, in Europe**; the second module is **1 kg liquid ammonia, partial oxidation, at plant, in Europe**. The third refers to **1 kg liquid ammonia, average, at regional storehouse, in Europe** and the fourth, to **1 kg liquid ammonia, average, at regional storehouse, in Switzerland**.

For the first and second modules the production of liquid ammonia with the steam reforming process and with the partial oxidation process, respectively, is considered. With the corresponding datasets generated for these processes, a third dataset „average liquid ammonia“ is prepared making a balanced average according the share of the mentioned production processes to the total European ammonia production.

All data are referred to 1 kg 100% liquid ammonia.

According to EFMA (2000) the typical plants considered for this study are the steam reforming plant and the partial oxidation plant as shown in Figure 1.1 and Figure 1.2, respectively.

In regard to the production capacity in the manufacturing plants, EFMA (2000) considers 1500 t.d⁻¹ a standard capacity. Capacities of 1800 t.d⁻¹ and above are common for new plants.

The system in both production processes includes the consumption of raw materials, auxiliaries, energy, infrastructure and land use as well as the generation of solid wastes and emissions to air and water. It also includes the transportation of raw materials, auxiliaries and wastes. Storage and transportation of the final product is not included in the first modules “at plant”, but in the modules “at regional storehouse”. The relationship between the four modules in Ecoinvent in regard to the production and storage of ammonia is shown in Fig. 11.3.

Carbon dioxide is the by-product generated in the manufacturing process.

For the study transient or unstable operations like starting-up or shuttings-down, are not included, but the production during stable operation conditions. The ammonia plant may stand-alone or integrated with other plants on the site, e.g. a urea plant, but such integration is not considered in this study.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to landfill.

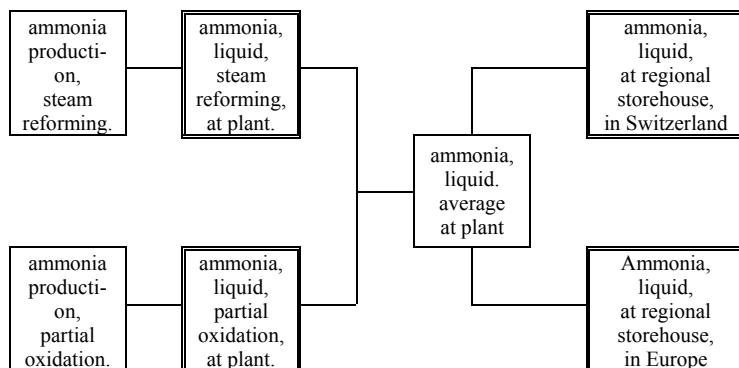


Fig. 11.3 Relationship between the four modules in Ecoinvent in regard to the production and storage of ammonia

11.5 Ammonia Production Processes

11.5.1 Ammonia, steam reforming

Data sources

Main data sources for this study are EFMA (2000) and Frischknecht (1999). Additional sources are Davis (1999), Patyk (1997) and Dones *et al.* (2007). UNEP (1998) is taken into account for plausibility checks and comparison reasons.

EFMA (2000) is a report on the best available techniques (BAT) for nitric acid production prepared in response to the proposed EU Directive on Integrated Pollution Prevention and Control (IPPC Directive). It considers basically the state-of-the-art of ammonia production in Europe. The document represents therefore a summary of information about present state as well as future improvements possible of the ammonia industry. The booklet was reviewed and updated by EFMA experts drawn from member companies. Nevertheless, no precise information about the origin of the data is available and therefore this is reflected in the uncertainty values. This source provides with average data from the industry as well as with achievable limits when using BAT.

Frischknecht (1999) is a Swiss survey providing with a life cycle assessment on ammonia, basing on literature (principally EFMA (1995)¹²) and own calculations. The survey analysis the production of ammonia in Europe by means of steam reforming and partial oxidation. The disadvantage of this high reliable source is that many of the numbers from EFMA (1995) are already updated.

Patyk (1997) analyses the material flow and the energy balance of different fertilisers, considering the situation in Germany, East Europe and the EU by analysing a broad spectrum of sources, like government reports, and diverse literature. Based on these sources and on his own calculations he presents tables with values for inputs and outputs from different fertiliser production processes. The disadvantage of this very complete source is that most of the information proceed from literature and not from recent data from nitric acid plants. Another feature from this survey is that it considers the burning of fuels and the corresponding emissions generated. For ammonia Patyk (1997) considers different literature data from Ullmann (1985), Ecoinvent (1994)¹³, Uhde (1991)¹⁴, Uhde (1994)¹⁵, Worrel (1994)¹⁶ and EFMA (1995), as well as personal communications. For this study his data referred to the EU are analysed.

UNEP (1998) has the purpose of "providing guidelines". The survey contains typical values based on BAT. The sources of information are not mentioned. Therefore, the values presented in this source are considered principally reference values.

Davis (1999) is a Compilation of Life Cycle Inventories of different fertiliser products used in Sweden and Western Europe. This survey provides with data based on measurements at manufacturing plants and considers also literature data. The chapter for ammonia bases mainly on data from Kongshaug (1998)¹⁷, EFMA (1995) and Ullmann (1985), as well as on personal communications. The data for Western Europe from this source are analysed. In the appendix it gives values for inputs and outputs of the manufacturing of ammonia, but considering also the extraction of hydrocarbons. Therefore, the appendix is not taken into account.

When information in the data sources is presented in ranges of values an average is taken and the amplitude of the range is indicated in the form of percent variability ($\pm\%$).

Raw materials and auxiliaries

The most relevant raw materials for the production of liquid ammonia by means of steam reforming are natural gas, air and water. Consumption of natural gas is considered in the next chapter.

In regard to auxiliaries, EFMA (2000) indicates for a BAT manufacturing plant a consumption of 3.00 E-05 kg solvents per kg ammonia produced ($\pm 30\%$). This source mentions also the consumption of usual treatment additives and regeneration agents at the boiler feedwater preparation units. No values are presented.

¹² EFMA (1995): European Fertilizer Manufacturers' Association (1995) Production of Ammonia. Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industries. Booklet N°1. Brussel

¹³ Ecoinvent (1994): Baumann T., Frischknecht R., Gränicher H.-P., Hofstetter P., Knoepfel I., Ménard M., Sprecher F. (1994) Ökoinventare für Energiesysteme: Grundlagen für den ökologischen Vergleich von Energiesystemen und den Einbezug von Energiesystemen in Ökobilanzen für die Schweiz. Im Auftrag des Bundesamtes für Energiewirtschaft und des Nationalen Energie-Forschungs-Fonds NEDD, Bern.

¹⁴ Uhde (1991): Uhde GmbH (1991) Energy-Efficient Ammonia Produktion. Enginering News 3-91, Dortmund.

¹⁵ Uhde (1994): Uhde GmbH (1994) Uhde's Ammonia Technology. Dortmund.

¹⁶ Worrel (1994): Worrel E. and Blok K. (1994) Energy Savings in the Nitrogen Fertilizer Industry in the Netherlands. Energy 19/2. 195-209.

¹⁷ Kongshaug (1998): Kongshaug G (1998) Energy Consumption and Greenhouse Gas Emissions in Fertilizer Production. Hydro-Agri Europe, Norway. EFMA (European Fertilizer Manufacturers'Association) Seminar on EU Legislation and the Legislation Process in the EU relative to Fertilizer, Prague, October 19-21 1998.

Catalysts based on cobalt-molybdenum, nickel, iron oxide/chromium oxide and copper oxide/zinc oxide are also mentioned (see also Section 1.3.1). Frischknecht (1999) mentions an average catalysts consumption of 3.50 E-04 kg per kg ammonia produced. In ecoinvent database there is no existing module for such catalysts as used in the ammonia production. Therefore, the input of catalyst is reported as “nickel, 95% at plant” as an approximation.

Tab. 11.2 gives an overview of the information about the consumption of water and air in the different sources used.

Tab. 11.2 Water and air consumption for the production of ammonia by means of steam reforming.

Input (kg ⁻¹ 100% NH ₃)		UNEP 1998	EFMA 2000	This study
water	m ³	1.10 E-03 ¹ (± 40%)	1.10 E-03 ¹ (± 40%)	1.10 E-03
air	kg	1.10 E+00 ^{2,3} (± 40%)	1.00 E+00 ³	1.50 E+00
		1.60 E+00 ^{2,4} (± 40%)	1.50 E+00 ⁴	
			2.00 E+00 ⁵	

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as (±%)

¹ Is variable, depending on operation of process condensate recycle. Cooling water is not included, variable from site to site. Value is the same for conventional- and excess air reforming

² Cooling air is not included. It is variable from site to site.

³ For conventional air reforming.

⁴ For excess air reforming.

⁵ For autothermal reforming.

Frischknecht (1999), basing on EFMA (1995), presents the same values for air and water consumption as EFMA (2000), and consequently is not included in the table. It seems that UNEP (1998) also bases on EFMA (1995).

Energy and transportation

The production of ammonia is a very energy demanding process. The heat demand has dropped significantly during the last thirty years but the process is still very energy consuming.

According to EFMA (2000), the total energy consumption for the production of ammonia in a modern steam reforming plant is 40-50% above the thermodynamic minimum. More than a half of the excess consumption is due to compression losses. The practical minimum consumption is assumed to be about 130% of the theoretical minimum. The process and energy systems are integrated to improve overall energy efficiency. Steam reforming ammonia plants have a high-level surplus heat available for steam production in the reforming, shift conversion and synthesis sections, and in the convection section of the primary reformer. Most of this waste heat is used for high-pressure steam production for use in turbines for driving the main compressors and pumps and as process steam extracted from the turbine system. A modern steam reforming ammonia plant can be made energetically self-sufficient if necessary, but usually a small steam export and electricity import are preferred.

EFMA (2000) states an energy requirement of 3.15 E+01 MJ LHV (Lower Heating Value) per kg NH₃ for a stand-alone plant with no energy export and no energy import except for feedstock and fuel. Based on literature and personal communications, Patyk (1997) considers 3.30 E+01 MJ.kg⁻¹ NH₃ an average value for energy consumption in the steam reforming process in Western Europe. Davis (1999) mentions an average energy consumption of 3.21 E+01 MJ for the production of ammonia currently in Western Europe by means of the steam reforming process, basing on data from Kongshaug (1998). Frischknecht (1999) considers 3.10 E+01 MJ LHV per kg NH₃ as an average input value.

UNEP (1998) states a total energy input of 3.35 E+01 MJ HHV (Higher Heating Value) per kg ammonia produced ($\pm 5\%$). This value corresponds for a stand-alone plant with no energy export and no energy import except for feedstock and fuel. According to this source, where auto-production of steam is insufficient and power is imported, the total energy consumption might be less.

In regard to steam export, EFMA (2000) states that modern steam reforming processes can be designed with no steam export or with some export of low/medium pressure steam if this can be favourably used on site. Steam export is usual in excess air reforming processes where the process air compressor is driven by a gas turbine, and in cases when electric power is used for driving one or more of the main compressors. Process with gas heated primary reforming may be designed for zero steam export even with some power import or gas turbine drive.

Concerning the energy demand and production of ammonia by means of steam reforming, Tab. 11.3 gives an overview of the reported energy balance in the different sources available.

Tab. 11.3 Energy inputs and outputs for the production of ammonia by means of steam reforming.

Input . kg ⁻¹ 100% NH ₃	UNEP 1998	EFMA 2000 ⁴	Davis 1999	Frischknecht 1999	This study
Natural gas MJ	2.45 E+01 ^{1, 2} 2.60 E+01 ^{1, 3}	2.21 E+01 ^{2, 5} 2.34 E+01 ^{3, 5} 2.48 E+01 ^{5, 6}		2.50 E+01 ⁴	2.34 E+01
Electricity fuel kWh MJ		8.10 E+00 ^{1, 2} ($\pm 10\%$) 6.30 E+00 ^{1, 3} ($\pm 15\%$) 5.40 E+00 ^{1, 6, 7} ($\pm 30\%$)	6.94 E-02 ⁸	6.00 E+00 ⁴	6.94 E-02 8.10 E+00

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as ($\pm\%$)
Values preceded with „—“ correspond to outputs

¹ Value corresponds to a stand-alone plant with no energy export and no energy import except for feedstock and fuel.

² For conventional steam reforming.

³ For excess air reforming.

⁴ Values correspond to Lower Heating Value.

⁵ For a modern plant.

⁶ For autothermal reforming.

⁷ The uncertainty is mainly due to the type of compressor drives.

⁸ Reported in the source as 0.25 MJ (conversion is done, considering 1 kWh = 3.6 MJ, according to Frischknecht *et al.* 2003b). Data from Van Balken 1998 ¹⁸.

The values presented by EFMA (2000) are taken, even if Frischknecht (1999) presents higher consumption values and although according to a conservative criterion, the latter could be seen as more appropriate. The reason for taking the numbers of EFMA (2000) is that Frischknecht (1999) considers actually BAT values too, only that these values -taken from EFMA (1995) - are older. EFMA (1995) presents lower numbers for consumption of energy than the following edition, i.e. EFMA (2000). This can be explained by five years of technology development and improvement of the environmental performance in the ammonia industry.

An average of the numbers from EFMA (2000) is used for this study, because it is not known how the different processes contribute currently to the overall production. Consequently, it is not possible to make a balancing average. On one hand, the most common process is presumably the conventional steam reforming. On the other hand, if only the values reported for this process were taken, the aver-

¹⁸ Van Balken H. (1998) Issue Manager, Technology, Environment and Safety, European Fertilizer Manufacturers' Association (EFMA). Personal communication.

age would show the best environmental performance possible. In turn, if an average is made, this resulting value reflects a slight lower environmental performance, probably closer to the real situation in the industry.

For this study, it is assumed that the fuel used in the production process is heavy fuel oil. In Ecoinvent database, heavy fuel oil is reported in kg. Thus, the amount of consumption of heavy fuel oil is 1.97 E-01 kg. $\text{kg}^{-1} \text{NH}_3$ (1kg heavy fuel oil = 41.2 MJ, according to Frischknecht et al. (2007b))

In Ecoinvent database natural gas is reported in cubic meters (m^3). Therefore, a conversion from MJ to m^3 is done, considering that 1 m^3 gas represents 36.3 MJ (Frischknecht et al. (2007b)). The value for Ecoinvent thus, is 6.45 E-01 m^3 natural gas per kg NH_3 produced.

Concerning transportation of raw materials and auxiliaries, no information about distances is available in the examined data sources. Therefore, for all raw materials and auxiliaries, standard distances as defined in Frischknecht et al. (2007b) were used: 100 km by lorry 32t and 600 km by train. For the transportation of the different wastes produced within the process it is assumed that they are sent to landfill and, again, standard distances are used: 10 km by lorry to disposal site. Additionally, it is assumed that this lorry has a capacity of 32 tonnes in order to facilitate the calculations of the total transport amounts for the database.

Tab. 11.4 summarises the total transport amounts for the production of 1 kg of ammonia by means of steam reforming.

Tab. 11.4 Total transport amounts for the production of ammonia by means of steam reforming.

(tkm. kg^{-1} 100% NH_3)	lorry	train
raw material	0	0
auxiliaries	3.80 E-05	2.28 E-04
waste to disposal sites	2.00 E-06	0
Total transports	4.00 E-05	2.28 E-04

Infrastructure and land-use

There is no information available about infrastructure and land-use of nitric acid plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. This estimated value is 4.00 E-10 unit. kg^{-1} chemical.

Production of Carbon Dioxide

EFMA (2000) mentions a production of 1.23 E+00 kg $\text{CO}_2 \cdot \text{kg}^{-1} \text{NH}_3$ for partial oxidation of residual oils ($\pm 5\%$). This value is also mentioned in Frischknecht (1999), quoting EFMA (1995). UNEP (1998) presents the same number, apparently basing on EFMA (1995) too. The value does not include the CO_2 in the flue gases. The variability depends on the degree of air reforming.

Emissions to air and water

According to EFMA (2000), the production of ammonia is relatively clean compared to many other chemical processes. During the normal operation of a reforming plant, only the NO_x and CO_2 emissions have to be considered. Generally the emissions from modern ammonia plants have little environmental impact.

According to the mentioned source, there is no emission of waste-heat, since this is virtually recycled in the process.

Emissions to air

The most important environmental impact owing to ammonia production is a large consumption of fossil fuel and emissions of fossil CO₂ as a consequence. The flue gas leaving the convection section is one of the main sources of emissions from the plant.

The following are the sources of emissions to air in the steam reforming process, according to EFMA (2000):

- Flue-gas from the primary reformer
- Vent gas from CO₂ removal
- Breathing gas from oil buffers (sales/compressors)
- Fugitive emissions (from flanges, stuffing boxes, etc.)
- Purge and flash gases from the synthesis section
- Non-continuous emissions (venting and flaring)

All the sources consulted mention the same emissions: mainly CO₂, NO_x, with small amounts of CO and SO₂, being the latter highly dependent on the type of fuel used. UNEP (1998) mentions also fugitive emissions of light hydrocarbons, H₂ and NH₃, that can occur due to leaks from flanges, stuffing boxes, maintenance work and catalyst handling.

The recovery of CO₂ for its further use reduces the emissions very considerably, but it depends on the needs of downstream facilities.

Emissions to water

According to EFMA 2000, pollution problems related to water may occur during normal operation due to process condensates or due to the scrubbing of waste gases containing ammonia. Without treatment process, condensate can contain up to 1.00 E-03 kg of NH₃ and 1.00 E-03 kg methanol per kg. More than 95% of the dissolved gases can be recovered by stripping with process steam and are recycled to the process. The stripped condensate can be re-used as boiler feedwater make-up after treatment by ion exchange. Total recycle is obtained in this way. In some cases the process condensate is used for feed-gas saturation and thus recycled to the process. Usually the ammonia absorbed from purge and flash gases is also recovered. Thus, emissions into water from the production during normal operation can be fully avoided. All available information about emissions to air and water is summarised in Tab. 11.5

Tab. 11.5 Emissions to air and water of the production of ammonia by means of steam reforming.

(kg.kg ⁻¹ 100% NH ₃)	UNEP 1998	EFMA 2000	Frischknecht 1999	This study
<i>Emission to air</i>				
NO _x (as NO ₂) ¹	9.50 E-04 ¹ (± 40%)	1.00 E-03 ⁵ 4.50 E-04 ⁶ 9.00 E-04 ⁷	1.00 E-03	1.00 E-03
N ₂ O				1.48 E-05
CH ₄ , fossil			1.2 E-05	1.2 E-05
CO ₂ , fossil	5.00 E-01 ^{2,3} 4.50 E-01 ^{2,4} (± 10%)	5.00 E-01 ^{2,5}	1.46 E+00	1.46 E+00
CO, fossil	< 3.00 E-05 ¹	< 3.00 E-05 ⁵	8.40 E-05	8.40 E-05
SO _x as SO ₂	< 1.00 E-05 ¹	< 1.00 E-05 ⁵	3.00 E-06	1.00 E-05
Particulates			1.20 E-06	1.20 E-06
NM VOC, unspecified			1.80 E-05	1.80 E-05
<i>Emission to water</i>				
NH ₃ or NH ₄ (as N)		1.00 E-04 ^{6,7}		1.00 E-04

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as (±%)

¹ The value is the same for conventional- and excess air reforming

² Value corresponding only to the CO₂ in the flue gas. The CO₂ recovered for its further use is not included.

³ For conventional air reforming.

⁴ For excess air reforming.

⁵ Typical emissions levels in a steam reforming plant with process condensate recycling. (Condensate recycled of 1.20 E+00 kg CO₂.kg⁻¹ NH₃)

⁶ Achievable values for new ammonia plants using BAT.

⁷ Achievable values for existing ammonia plants using BAT.

For the emissions, the highest value is taken, considering EFMA (2000) and Frischknecht (1999). Both present values corresponding to a mix of fuel plus process emissions. For NO_x, the highest value reported by EFMA 2000 is taken. The same value is presented in Frischknecht 1999. Also for SO_x the number from EFMA 2000 is taken. This number, reported as maximal value is taken as an average value, according to a conservative criterion. For CH₄, CO₂, CO and Particulates, the values from Frischknecht are used. Particulate matter is reported in ecoinvent database in three fractions: Particulates, < 2.5 um; Particulates, > 2.5 um and < 10 um and Particulates, > 10 um. According to Berdowski *et al.* (2002) and considering that the values of particulates correspond principally (99%) to the burning of heavy fuel oil, it is assumed that the distribution is 71% for the first mentioned fraction, 15% for the second and 14% for the last. On this base, the corresponding value for each fraction is calculated. Therefore, the following values are used in this study:

$$8.52 \text{ E-07 kg Particulates (< 2.5 um)} .\text{kg}^{-1} \text{NH}_3,$$

$$1.80 \text{ E-07 kg Particulates (> 2.5 um and < 10 um)} .\text{kg}^{-1} \text{NH}_3, \text{ and}$$

$$1.68 \text{ E-07 kg Particulates (> 10 um)} .\text{kg}^{-1} \text{NH}_3.$$

Additional emissions from the burning of fuels are estimated from the inventories of the respective heating systems in Dones *et al.* (2007). The respective procedure is described in chapter 5.2 of the paper & board part in Hischier (2007). Tab. 11.6 summarises the calculated data for these additional air emissions based on the fuel mix used here.

Tab. 11.6 Additional air emissions from the fuel mix used for ammonia from steam reforming process

[per kg product]	Total	[per kg product]	Total	[per kg product]	Total
Heat, waste	MJ	3.47E+01	Cobalt	kg	2.67E-07
Carbon dioxide, biogenic	kg	-	Copper	kg	3.97E-07
Carbon dioxide, fossil	kg	1.94E+00	Dinitrogen monoxide	kg	1.53E-05
Carbon monoxide, biogenic	kg	-	Dioxins, measured as 2,3,7,8-tetrachloro	kg	4.35E-15
Carbon monoxide, fossil	kg	1.06E-04	Ethane	kg	-
Nitrogen oxides	kg	1.23E-03	Ethanol	kg	2.43E-06
Particulates, < 2.5 um	kg	2.88E-04	Ethene	kg	-
Particulates, > 10 um	kg	8.10E-05	Ethyne	kg	-
Particulates, > 2.5 um, and < 10um	kg	4.05E-05	Fluorine	kg	-
Sulfur dioxide	kg	3.25E-03	Formaldehyde	kg	5.99E-06
Acetic acid	kg	8.37E-06	Hydrocarbons, aliphatic, alkanes, unsp	kg	4.86E-06
Acetaldehyde	kg	1.24E-06	Hydrocarbons, aliphatic, unsaturated	kg	2.43E-07
Acetone	kg	1.22E-06	Hydrocarbons, aromatic	kg	1.22E-06
Ammonia	kg	8.10E-08	Hydrogen chloride	kg	1.17E-05
Aluminum	kg	-	Hydrogen fluoride	kg	1.17E-06
Antimony	kg	-	Hydrogen sulfide	kg	-
Arsenic	kg	1.05E-07	Iodine	kg	-
Barium	kg	-	Iron	kg	1.46E-06
Benzene	kg	9.36E-06	Lead	kg	4.62E-07
Benzene, ethyl-	kg	-	Lead-210	kBq	-
Benzene, hexachloro-	kg	-	Magnesium	kg	-
Benzo(a)pyrene	kg	4.61E-10	Manganese	kg	-
Beryllium	kg	-	Mercury	kg	1.92E-09
Boron	kg	-	Methane, biogenic	kg	-
Bromine	kg	-	Methane, fossil	kg	7.11E-05
Butane	kg	1.64E-05	Methanol	kg	4.13E-06
Calcium	kg	6.48E-07	Molybdenum	kg	1.30E-07
Cadmium	kg	2.67E-07	m-Xylene	kg	-
Chlorine	kg	-	Nickel	kg	5.27E-06
Chromium	kg	1.28E-07	NM VOC, non-methane volatile organic	kg	-
Chromium VI	kg	1.30E-09	PAH, polycyclic aromatic hydrocarbons	kg	2.39E-07

Solid wastes

EFMA (2000) indicates that the BAT ammonia process does not normally produce solid wastes. The sources consulted report on the generation of spent catalysts and molecular sieves. They state that these wastes are of minor importance since they are often recycled to a large extent.

UNEP (1998) mentions an achievable value of 1.00 E-04 kg spent catalyst per kg ammonia produced, when using BAT. For solid wastes generated at a BAT plant, EFMA (2000) presents a value of 2.00 E-04 kg. kg⁻¹ NH₃. This last value is taken for this study, according to a conservative criterion.

For this study, solid waste is reported as “disposal, municipal solid waste, 22.9 %water, to sanitary landfill”, due to lack of further information about the composition of the wastes mentioned. This is considered the most appropriate among the different modules available in the database.

11.5.2 Ammonia, partial oxidation

Data sources

Similar sources like for ammonia, steam reforming (see chapter 11.5.1)

Raw materials and auxiliaries

In regard to consumption of water and air, EFMA reports a consumption of 1.20 E-03 m³ water and 4.00 E+00 kg air per kg ammonia produced. Cooling water and cooling air are not included in these numbers, being variable from site to site. Frischknecht (1999), basing on EFMA (1995), presents the same values as EFMA (2000). UNEP (1998) mentions also the same values, seeming to base on EFMA (1995) too.

In regard to auxiliaries, the same numbers for solvents are considered as for steam reforming ($3.00 \text{ E-}05 \text{ kg. kg}^{-1} \text{ NH}_3$).

Energy and transportation

As for steam reforming, the process and energy systems are integrated to improve overall energy efficiency. Auxiliary boilers are required if the compressors are steam-driven.

Davis (1999) mentions an average energy consumption of 4.10 E+01 to $4.90 \text{ E+01} \text{ MJ}$ for the production of ammonia in Western Europe by means of the partial oxidation process, basing on data from Kongshaug (1998). UNEP (1998) states a total energy input of $4.20 \text{ E+01} \text{ MJ}$ (HHV Value) per kg ammonia produced ($\pm 7\%$), including in this value the import of power and/or auxiliary steam. Patyk (1997) considers $3.63 \text{ E+01} \text{ MJ.kg}^{-1} \text{ NH}_3$ an average value for energy consumption in the partial oxidation process. Frischknecht (1999) considers $3.10 \text{ E+01} \text{ MJ LHV .kg}^{-1} \text{ NH}_3$ as an average input value. The partial oxidation has a steam deficit if all compressors are steam-driven (EFMA (2000)).

Concerning the energy demand and production of the production of ammonia by means of partial oxidation, Tab. 11.7 gives an overview of the reported energy balance in the different sources available.

Tab. 11.7 Energy inputs and outputs for the production of ammonia by means of partial oxidation.

Input . kg $^{-1}$ 100% NH $_3$	UNEP 1998	EFMA 2000	Frischknecht 1999	This study
FEEDSTOCK MJ	3.20 E+01	2.88 E+01 ¹	3.20 E+01 ³	2.88 E+01
Electricity fuel MJ		7.20 E+00 ² ($\pm 25\%$)	$8.00 \text{ E-}01$ ³	$7.20 \text{ E-}01$⁴
			7.20 E+00 ³	6.48 E+00⁴

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as ($\pm\%$)
Values preceded with „–“ correspond to outputs

¹ For a modern plant. Value corresponds to Lower Heating Value.

² Value corresponds to a stand-alone plant with no energy export and no energy import except for feedstock and fuel. Value corresponds to Lower Heating Value.

³ Lower Heating Value.

⁴ Assuming that 10% of the energy ($7.20 \text{ E+00} \text{ MJ.kg}^{-1}$) is imported as electricity and 90% from fuel.

The values presented by EFMA (2000) are taken, even if Frischknecht (1999) presents higher consumption values and according to a conservative criterion, the latter could be seen as more appropriate. The reason for taking the numbers of EFMA (2000) is that Frischknecht (1999) considers actually BAT values too, only that these values -taken from EFMA (1995) – are older. EFMA (1995) presents lower numbers for consumption of energy than the following edition, i.e. EFMA (2000). This can be explained by five years of technology development and improvement of the environmental performance in the ammonia industry.

For this study, it is assumed that both the feedstock and the fuel are heavy fuel oil. Both values are added.

Taking into consideration that sometimes an electricity import is necessary, and in concordance with Frischknecht (1999), it is assumed that 10% of the overall amount of energy provided by the fuel corresponds to electricity consumption and 90% to heavy fuel oil. Consequently, the value for fuel from EFMA is taken ($7.20 \text{ E+00} \text{ MJ}$), but only 90% is reported as heavy fuel oil consumption and the remaining 10% is reported as energy supplied as electricity.

For heavy fuel oil, a conversion is necessary in order to report it in kg in Ecoinvent database. Thus, the value for Ecoinvent is $8.57 \text{ E-}01 \text{ kg fuel oil per kg ammonia produced}$. This is the result of adding

28.8 MJ fuel oil for feedstock and 6.48 MJ for fuel (90% of 7.20 MJ), and converting the resulting value into kg, considering 1 kg fuel oil = 41.2 MJ, according to Frischknecht et al. (2007b).

A conversion is also necessary for electricity, since in Ecoinvent database this input is reported in kWh. Thus, the value for Ecoinvent is 2.00 E-01 kWh kg ammonia produced (1 kWh = 3.6 MJ, according to Frischknecht et al. (2007b)).

In regard to transportation, the same considerations and assumptions as for steam reforming ammonia are to be taken into account. Tab. 11.8 summarises the total transport amounts for the production of 1 kg of ammonia by means of steam reforming.

Tab. 11.8 Total transport amounts for the production of ammonia by means of partial oxidation.

(tkm. kg ⁻¹ 100% NH ₃)	lorry	train
raw material	0	0
auxiliaries	3.00 E-06	1.80 E-05
waste to disposal sites	2.00 E-06	0
Total transports	5.00 E-06	1.80 E-05

Infrastructure and land use

Same considerations as for ammonia, steam reforming.

Production of Carbon Dioxide

EFMA (2000) mentions a production of 2.30 E+00 kg CO₂.kg⁻¹ NH₃ for partial oxidation of residual oils (\pm 15%). This value is also mentioned in Frischknecht (1999), quoting EFMA (1995). UNEP (1998) presents the same number, apparently basing on EFMA (1995) too. The value does not include the CO₂ in the flue gases.

Emissions to air and water

According to EFMA (2000), the production of ammonia is relatively clean compared to many other chemical processes. Generally the emissions from modern ammonia plants have little environmental impact. In partial oxidation plants with oil-fired auxiliary boilers the emission of SO₂ are of relevance, but using low sulphur fuel oil can reduce it.

Emissions to air

According to EFMA (2000), the partial oxidation process has the same emission sources as described for the reforming process except for the primary reformer flue-gas. A partial oxidation plant may also have auxiliary boiler(s) for power steam production if more efficiently off-site produced power is not available. The fuel to the auxiliary boiler/superheater together with possible scrubbing equipment determines the amount of CO₂ in the flue-gas. Tail gas from sulphur recovery will also contain sulphur oxides. This means that the CO₂ emission from partial oxidation plants is higher than in the reformer flue-gas. Other additional emissions may be H₂S, methanol, CO and dust traces. NO_x emission depends on operational parameters at the primary reformer and the nitrogen content of the fuel. Excess nitrogen is usually vented.

When using steam-driven compressors, the flue-gas from the auxiliary boilers is the main source of emissions. These are mainly SO₂, NO_x and CO₂. The site emissions are very low if the compressors are driven by imported electric power (EFMA (2000))

UNEP (1998) states that the emissions to air vary depending on the fuel and feedstock, and recovery procedures. The emissions of CO₂ are highly dependent on the type of fuel. According to this source, fugitive emissions of light hydrocarbons, H₂, NH₃, CO and CO₂ can occur due to leaks from flanges, stuffing boxes, maintenance work and catalyst handling.

The recovery of CO₂ for its further use reduces the emissions very considerably, but it depends on the needs of downstream facilities.

In regard to sulphur-containing emissions, EFMA (2000) states that in BAT partial oxidation most (87-95%) of the sulphur content of the feed to the gasifier is recovered in the Claus unit.

Emissions to water

Same considerations as for steam reforming. For partial oxidation, EFMA (2000) mentions additionally that soot and ash removal may cause pollution problems if not properly handled. Soot from gasification in partial oxidation is usually recovered and recycled to the process. Traces of soot and slag are emitted to water. All available information about emissions to air and water is summarised in Tab. 11.9.

Tab. 11.9 Emissions to air and water of the production of ammonia by means of partial oxidation.

(kg.kg ⁻¹ 100% NH ₃)	UNEP 1998	EFMA 2000	Frischknecht 1999	This study
<i>Emission to air</i>				
NO _x (as NO ₂)		4.50 E-04 ¹ 9.00 E-04 ²	1.20 E-03	1.20 E-03
N ₂ O				5.49 E-05
CH ₄ , fossil			2.20 E-05	2.20 E-05
CO ₂ , fossil			2.34 E+00	2.34 E+00
CO, fossil	< 1.30 E-04		2.20 E-04	2.20 E-04
SOx as SO ₂	2.00 E-03 (± 100%)		1.26 E-02	1.26 E-02
Particulates			4.60 E-04	4.60 E-04
H ₂ S			1.40 E-06	1.40 E-06
Methanol			4.00 E-04	4.00 E-04
NMVOC, unspecified			2.20 E-05	2.20 E-05
<i>Emission to water</i>				
NH ₃ or NH ₄ (as N)		1.00 E-04 ^{1,2}		1.00 E-04

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as (±%)

¹ Achievable values for new ammonia plants using BAT.

² Achievable values for existing ammonia plants using BAT.

The same criteria for the election of values are used as for steam reforming. According to Berdowski *et al.* 2002 and considering that the values of particulates correspond to the burning of heavy fuel oil, it is assumed that the distribution is 71% for the first mentioned fraction, 15% for the second and 14% for the last. On this base, the corresponding value for each fraction is calculated. Therefore, the following values are used in this study:

$$3.27 \text{ E-04 kg Particulates } (< 2.5 \text{ um}) \cdot \text{kg}^{-1} \text{ NH}_3,$$

$$6.90 \text{ E-05 kg Particulates } (> 2.5 \text{ um and } < 10 \text{ um}) \cdot \text{kg}^{-1} \text{ NH}_3, \text{ and}$$

$$6.44 \text{ E-05 kg Particulates } (> 10 \text{ um}) \cdot \text{kg}^{-1} \text{ NH}_3.$$

Additional emissions from the burning of fuels are estimated from the inventories of the respective heating systems in Dones et al. (2007). The respective procedure is described in chapter 5.2 of the paper & board part in Hischier (2007). Tab. 11.10 summarises the calculated data for these additional air emissions based on the fuel mix used here.

Tab. 11.10 Additional air emissions from the fuel mix used for ammonia from partial oxidation process

[per kg product]	Total	[per kg product]	Total	[per kg product]	Total
Heat, waste	MJ 3.88E+01	Cobalt	kg 1.17E-06	Pentane	kg -
Carbon dioxide, biogenic	kg -	Copper	kg 1.73E-06	Phenol	kg -
Carbon dioxide, fossil	kg 2.75E+00	Dinitrogen monoxide	kg 5.65E-05	Phenol, pentachloro-	kg -
Carbon monoxide, biogenic	kg -	Dioxins, measured as 2,3,7,8-tetrachloro	kg 1.59E-14	Phosphorus	kg -
Carbon monoxide, fossil	kg 2.47E-04	Ethane	kg -	Polonium-210	kBq -
Nitrogen oxides	kg 3.53E-03	Ethanol	kg 1.06E-05	Potassium	kg -
Particulates, < 2.5 µm	kg 1.24E-03	Ethene	kg -	Potassium-40	kBq -
Particulates, > 10 µm	kg 3.53E-04	Ethyne	kg -	Propane	kg 1.06E-06
Particulates, > 2.5 µm, and < 10µm	kg 1.77E-04	Fluorine	kg -	Propene	kg -
Sulfur dioxide	kg 1.41E-02	Formaldehyde	kg 1.59E-05	Propionic acid	kg -
Acetic acid	kg 2.12E-05	Hydrocarbons, aliphatic, alkanes, unsp	kg 2.12E-05	Radium-226	kBq -
Acetaldehyde	kg 5.30E-06	Hydrocarbons, aliphatic, unsaturated	kg 1.06E-06	Radium-228	kBq -
Acetone	kg 5.30E-06	Hydrocarbons, aromatic	kg 5.30E-06	Radon-220	kBq -
Ammonia	kg 3.53E-07	Hydrogen chloride	kg 5.08E-05	Radon-222	kBq -
Aluminum	kg -	Hydrogen fluoride	kg 5.08E-06	Scandium	kg -
Antimony	kg -	Hydrogen sulfide	kg -	Selenium	kg 4.24E-07
Arsenic	kg 4.59E-07	Iodine	kg -	Silicon	kg -
Barium	kg -	Iron	kg 6.36E-06	Sodium	kg 2.65E-05
Benzene	kg -	Lead	kg 2.01E-06	Strontium	kg -
Benzene, ethyl-	kg -	Lead-210	kBq -	Thallium	kg -
Benzene, hexachloro-	kg -	Magnesium	kg -	Thorium	kg -
Benzo(a)pyrene	kg 9.89E-10	Manganese	kg -	Thorium-228	kBq -
Beryllium	kg -	Mercury	kg 5.30E-09	Thorium-232	kBq -
Boron	kg -	Methane, biogenic	kg -	Tin	kg -
Bromine	kg -	Methane, fossil	kg 1.06E-04	Titanium	kg -
Butane	kg -	Methanol	kg 1.80E-05	Toluene	kg 1.06E-06
Calcium	kg 2.82E-06	Molybdenum	kg 5.65E-07	Uranium	kg -
Cadmium	kg 1.17E-06	m-Xylene	kg -	Uranium-238	kBq -
Chlorine	kg -	Nickel	kg 2.30E-05	Vanadium	kg 9.18E-05
Chromium	kg 5.58E-07	NMVOCS, non-methane volatile organic	kg -	Xylene	kg -
Chromium VI	kg 5.65E-09	PAH, polycyclic aromatic hydrocarbons	kg 2.05E-08	Zinc	kg 1.41E-06

Solid wastes

Same considerations as for steam reforming. The same value as for steam reforming is taken (2.00 E-04 kg. kg⁻¹ NH₃), according to EFMA (2000).

In partial oxidation plants, sulphur is recovered in the Claus unit and can be used as a feedstock in sulphuric acid units. The ash can be upgraded and used as an ore substitute.

11.6 Average European Ammonia

According to IFA (2003), about three quarters of world ammonia production is based on natural gas. (This proportion is 85% if excluding the numerous small, coal-burning plants in China). The mentioned resource reports a world annual production of 141 Mt. 1989, from which 12.7 Mt. corresponds to Europe. Frischknecht (1999) mentions for the production in 1990 in Western Europe a value of 13,5 Mt.

According to Frischknecht (1999), in Western Europe 72% steam and 13% naphtha were used in the year's 1982/1983 for the production of ammonia. For this study, and in concordance to Frischknecht (1999), it is assumed that a representative distribution of the production means for Europe is 85% steam reforming and 15% partial oxidation (of heavy fuel oil)

The modules ammonia at storehouse refer to an average ammonia and base on the balanced averages from the numbers of both process discussed, considering that steam reforming ammonia contributes with 85% and partial oxidation with 15% to the average value. For the uncertainties scores, the ones

corresponding to steam reforming are used, since the relevance of this process -and therefore of its numbers- is higher.

11.7 Ammonia at Regional Storehouse

For the modules concerning ammonia at regional storehouses, both in Europe and in Switzerland, transportation and storage of the final product ammonia is considered.

According to EFMA (2000), in a refrigerated storage, the cold losses are balanced by recompressing and recondensing the evaporated ammonia. During recompression, some inerts containing also traces of ammonia cannot be condensed but must be flared or scrubbed with water. Small continuous emissions may thus occur, in addition to minor non-continuous emissions during loading operations. Nevertheless, no values regarding emissions related to the storage or transportation of ammonia are available in the sources consulted. Thus, only additional transportation is taken into consideration for the modules at regional storehouse but no other inputs or outputs.

For transportation and due to the lack of data, standard distances as presented in Frischknecht et al. (2007b) are used: 50 km by lorry 32t and 600 km by train. Thus, for the transportation of 1 kg liquid ammonia to a regional storehouse in Europe, 1.00 E-01 tkm by lorry 32t and 6.00 E-01 tkm by rail are used. If considering a Swiss regional lager, the values are 5.00 E-02 tkm by lorry 28t and 6.00 E-01 tkm by rail per kg liquid ammonia.

11.8 Data Quality Considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

Most of the used data for the principal emissions and for energy consumption are extracted from EFMA (2000). The main concern in regard to EFMA (2000) is that it does not mention on how many different sample points the different values given are based, if these are measures or estimations and to what period of time these correspond. All the mentioned factors leads to higher uncertainty scores. Other outputs, as well as numbers for catalysts consumption are taken from Frischknecht (1999). This source bases on literature (principally EFMA (1995)) and own calculations. The disadvantage of this high reliable source is that many of the numbers from EFMA (1995) are already updated.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht et al. (2007b) (transport) resp. the very general module of an organic chemical plant are used. The module analysed corresponds to Europe. However, the data used for this study correspond not only to whole Europe but also to the EU or Western Europe. This lack of representativeness is reflected in the uncertainty scores.

Tab. 11.11 and Tab. 11.12 summarise the input and output data as well as the uncertainties used for the production of ammonia by means of steam reforming and partial oxidation, respectively. The values are given for the production of 1 kg of 100% liquid ammonia.

Tab. 11.13 and Tab. 11.14 show the inputs and outputs data as well as the uncertainties related to the transportation and storage of liquid ammonia to a regional storehouse in Europe and in Switzerland, respectively. As mentioned above, a balanced average has been calculated considering that steam reforming contributes with 85% and partial oxidation with 15% to the total. The values are given for the production of 1 kg of 100% liquid ammonia.

Tab. 11.11 Input- / Output-data for the ammonia production by means of steam reforming (expressed per kg ammonia produced)

Explanation	Name	Location	Unit	ammonia, steam reforming, liquid, at plant		UncertaintyType pe StandardDeviation at95%	GeneralComment		
				RER 0 kg					
				InfrastructureProcess					
				Unit					
Resources	Water, unspecified natural origin		m3	1.10E-3	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
Input from Technosphere	solvents, organic, unspecified, at plant	GLO	kg	3.00E-5	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
	nickel, 99.5%, at plant	GLO	kg	3.50E-4	1	1.26	(3.2,1.1,1.5); data from survey from literature (Frischknecht 1999)		
	natural gas, high pressure, at consumer	RER	MJ	2.34E+1	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
	heavy fuel oil, at regional storage	RER	kg	1.97E-1	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	6.94E-2	1	1.22	(3.2,1.1,1.5); data from survey from literature (Davis 1999)		
	transport, lorry 32t	RER	tkm	4.00E-5	1	2.05	(4,na,na,na,na); Standard distances		
	transport, freight, rail	RER	tkm	2.28E-4	1	2.05	(4,na,na,na,na); Standard distances		
	chemical plant, organics disposal, municipal solid waste, 22.9% water, to sanitary landfill	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); Estimation		
		CH	kg	2.00E-4	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
OUTPUTS	ammonia, steam reforming, liquid, at plant	RER	kg	1.00E+0	1				
water emission	Nitrogen		kg	1.00E-4	1	1.58	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
air emission	Nitrogen oxides		kg	1.00E-3	1	1.58	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
	Methane, fossil		kg	1.20E-5	1	1.59	(3.2,1.1,1.5); data from survey from literature (Frischknecht 1999)		
	Carbon dioxide, fossil		kg	1.46E+0	1	1.26	(3.2,3,1.1,1.5); data from survey from literature (Frischknecht 1999)		
	Carbon monoxide, fossil		kg	8.40E-5	1	5.08	(3.2,3,1.1,1.5); data from survey from literature (Frischknecht 1999)		
	Sulfur dioxide		kg	1.00E-5	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
	Heat, waste		MJ	3.47E+1	1	1.26	(3.2,3,1.1,1.5); calculated, based on fuel & electricity input		
	Particulates, < 2.5 um		kg	2.88E-4	1	3.32	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Particulates, > 10 um		kg	8.10E-5	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Particulates, > 2.5 um, and < 10um		kg	4.05E-5	1	2.29	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Acetic acid		kg	8.37E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Acetaldehyde		kg	1.24E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Acetone		kg	1.22E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Ammonia		kg	8.10E-8	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Arsenic		kg	1.05E-7	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Benzene		kg	9.36E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Benzo(a)pyrene		kg	4.61E-10	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Butane		kg	1.64E-5	1	3.32	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Calcium		kg	6.48E-7	1	3.32	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Cadmium		kg	2.67E-7	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Chromium		kg	1.28E-7	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Chromium VI		kg	1.30E-9	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Cobalt		kg	2.67E-7	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Copper		kg	3.97E-7	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Dinitrogen monoxide		kg	1.53E-5	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin		kg	4.35E-15	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Ethanol		kg	2.43E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Formaldehyde		kg	5.99E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrocarbons, aliphatic, alkanes, unspecified		kg	4.88E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrocarbons, aliphatic, unsaturated		kg	2.43E-7	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrocarbons, aromatic		kg	1.22E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrogen chloride		kg	1.17E-5	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrogen fluoride		kg	1.17E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Iron		kg	1.46E-6	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Lead		kg	4.62E-7	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Mercury		kg	1.92E-9	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Methanol		kg	4.13E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Molybdenum		kg	1.30E-7	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Nickel		kg	5.27E-6	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	PAH, polycyclic aromatic hydrocarbons		kg	2.39E-7	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Pentane		kg	2.81E-5	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Propane		kg	4.92E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Propionic acid		kg	4.68E-7	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Selenium		kg	9.72E-8	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Sodium		kg	6.08E-6	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Toluene		kg	4.92E-6	1	1.88	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Vanadium		kg	2.11E-5	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		
	Zinc		kg	3.24E-7	1	5.37	(2.5,2,1.4,5); estimation, based on industrial heating modules of energy carriers used		

Tab. 11.12 Input- / Output-data for the ammonia production by means of partial oxidation (expressed per kg ammonia produced)

Explanation	Name	Location	Unit	ammonia, partial oxidation, liquid, at plant	RER 0 kg	UncertaintyType	StandardDeviation95%	GeneralComment	
								Infrastructure	Process
								Unit	Unit
Resources Input from Technosphere	Water, unspecified natural origin		m3	1.20E-3	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
	solvents, organic, unspecified, at plant	GLO	kg	3.00E-5	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
	heavy fuel oil, at regional storage	RER	kg	8.57E-1	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	2.00E-1	1	1.26	(3.2,1.1,1.5); data from survey from literature (Frischnecht 1999)		
	transport, lorry 32t	RER	tkm	5.00E-6	1	2.05	(4,na,na,na,na); Standard distances		
	transport, freight, rail	RER	tkm	1.80E-5	1	2.05	(4,na,na,na,na); Standard distances		
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1.5,3.5,4); Estimation		
	disposal, municipal solid waste, 22.9% water, to sanitary landfill	CH	kg	2.00E-4	1	1.24	(3.2,1.1,1.5); data from survey from literature (EFMA 2000)		
	ammonia, partial oxidation, liquid, at plant	RER	kg	1.00E+0					
Output									
water emission	Nitrogen		kg	1.00E-4	1	1.58	(3,2,1,1,1.5); data from survey from literature (EFMA 2000)		
air emission	Nitrogen oxides		kg	1.20E-3	1	1.59	(3,2,3,1,1.5); data from survey from literature (Frischnecht 1999)		
	Methane, fossil		kg	2.20E-5	1	1.59	(3,2,3,1,1.5); data from survey from literature (Frischnecht 1999)		
	Carbon dioxide, fossil		kg	2.34E+0	1	1.26	(3,2,3,1,1.5); data from survey from literature (Frischnecht 1999)		
	Carbon monoxide, fossil		kg	2.20E-4	1	5.08	(3,2,3,1,1.5); data from survey from literature (Frischnecht 1999)		
	Sulfur dioxide		kg	1.26E-2	1	1.26	(3,2,3,1,1.5); data from survey from literature (Frischnecht 1999)		
	Hydrogen sulfide		kg	1.40E-6	1	1.59	(3,2,3,1,1.5); data from survey from literature (Frischnecht 1999)		
	Methanol		kg	4.00E-4	1	1.59	(3,2,3,1,1.5); data from survey from literature (Frischnecht 1999)		
	Heat, waste		MJ	3.96E+1	1	1.26	(3,2,3,1,1.5); calculated, based on fuel & electricity input		
	Particulates, < 2.5 um		kg	1.24E-3	1	3.32	(2,5,2,1,4,5); calculated, based on industrial heating modules of energy carriers used		
	Particulates, > 10 um		kg	3.53E-4	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Particulates, > 2.5 um, and < 10um		kg	1.77E-4	1	2.29	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Acetic acid		kg	2.12E-5	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Acetaldehyde		kg	5.30E-6	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Acetone		kg	5.30E-6	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Ammonia		kg	3.53E-7	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Arsenic		kg	4.59E-7	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Benz(a)pyrene		kg	9.89E-10	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Calcium		kg	2.82E-6	1	3.32	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Cadmium		kg	1.17E-6	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Chromium		kg	5.58E-7	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Chromium VI		kg	5.65E-9	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Cobalt		kg	1.17E-6	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Copper		kg	1.73E-6	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Dinitrogen monoxide		kg	5.65E-5	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin		kg	1.59E-14	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Ethanol		kg	1.06E-5	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Formaldehyde		kg	1.59E-5	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrocarbons, aliphatic, alkanes, unspecified		kg	2.12E-5	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrocarbons, aliphatic, unsaturated		kg	1.06E-6	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrocarbons, aromatic		kg	5.30E-6	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrogen chloride		kg	5.08E-5	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Hydrogen fluoride		kg	5.08E-5	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Iron		kg	6.36E-6	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Lead		kg	2.01E-6	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Mercury		kg	5.30E-9	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Molybdenum		kg	5.65E-7	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Nickel		kg	2.30E-5	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	PAH, polycyclic aromatic hydrocarbons		kg	2.05E-8	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Propane		kg	1.06E-6	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Selenium		kg	4.24E-7	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Sodium		kg	2.65E-5	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Toluene		kg	1.06E-6	1	1.88	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Vanadium		kg	9.18E-5	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		
	Zinc		kg	1.41E-6	1	5.37	(2,5,2,1,4,5); estimation, based on industrial heating modules of energy carriers used		

Tab. 11.13 Input- / Output-data for liquid ammonia at regional storehouse, Europe¹. (expressed per kg ammonia produced)

Explanation	Name	Location	Unit	ammonia, liquid, at regional storehouse	RER 0 kg	UncertaintyType	StandardDeviation95%	GeneralComment	
								Infrastructure	Process
								Unit	Unit
Input from Technosphere	ammonia, steam reforming, liquid, at plant	RER	kg	8.50E-1	1	2.11	(3,1,1,1,3,5); estimation based on literature		
	ammonia, partial oxidation, liquid, at plant	RER	kg	1.50E-1	1	2.11	(3,1,1,1,3,5); estimation based on literature		
	transport, lorry 32t	RER	tkm	1.00E-1	1	2.05	(4,na,na,na,na,na); Standard distances		
	transport, freight, rail	RER	tkm	6.00E-1	1	2.05	(4,na,na,na,na,na); Standard distances		
Output	ammonia, liquid, at regional storehouse	RER	kg	1					

¹ Balanced average of values for steam reforming (85%) and partial oxidation (15%).

Tab. 11.14 Input- / Output-data for liquid ammonia at regional storehouse, Switzerland¹. (expressed per kg ammonia produced)

Explanation	Name	Location	Unit	ammonia, liquid, at regional storehouse	UncertaintyType	StandardDeviation95	GeneralComment
	Location			CH			
	InfrastructureProcess			0		%	
Input from Technosphere	ammonia, steam reforming, liquid, at plant	RER	kg	8.50E-1	1	2.11	(3,1,1,1,3,5); estimation based on literature
	ammonia, partial oxidation, liquid, at plant	RER	kg	1.50E-1	1	2.11	(3,1,1,1,3,5); estimation based on literature
	transport, lorry 32t	RER	tkm	1.00E-1	1	2.05	(4,na,na,na,na,na); Standard distances
	transport, freight, rail	RER	tkm	6.00E-1	1	2.05	(4,na,na,na,na,na); Standard distances
Output	ammonia, liquid, at regional storehouse	CH	kg	1			

¹ Balanced average of values for steam reforming (85%) and partial oxidation (15%).

11.9 Cumulative Results and Interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

11.10 Conclusions

Average European datasets for the production of ammonia by both production ways (steam reforming and partial oxidation) for the year 2000 are established. Furthermore, datasets representing a weighted mix of the different technologies are established as well (“at regional storage” – datasets).

All these datasets are in accordance with the present quality guidelines of the ecoinvent project and are based on a report covering the European industry, based on statistics from the area 1995 to 2000. The data are thus of a good quality and can be used in a very broad context.

11.11 EcoSpold Meta Information

ReferenceFunction	Name	ammonia, steam reforming, liquid, at plant	ammonia, partial oxidation, liquid, at plant	ammonia, liquid, at regional storehouse	ammonia, liquid, at regional storehouse
Geography	Location	RER	RER	RER	CH
ReferenceFunction	InfrastructureProcess	0	0	0	0
ReferenceFunction	Unit	kg	kg	kg	kg
ReferenceFunction	LocalName	Ammoniak, Dampfreformierung, flüssig, ab Werk	Ammoniak, Partielle Oxidation, flüssig, ab Werk	Ammoniak, Durchschnitt, flüssig, ab Regionallager	Ammoniak, Durchschnitt, flüssig, ab Regionallager
ReferenceFunction	Synonyms				
ReferenceFunction	GeneralComment	Manufacturing process starting with natural gas, air and electricity is considered, plus auxiliaries, energy, transportation, infrastructure and land use, as well as wastes and emissions into air and water. Transport of the raw materials, auxiliaries and wastes is included, transport and storage of the product are not included. Carbon Dioxide is the byproduct generated. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Values are taken principally from EFMA 2000 and Frischknecht 1999 (see report). Inventory refers to 1 kg 100% ammonia, liquid, at plant.	Manufacturing process starting with heavy fuel oil, air and electricity is considered, plus auxiliaries, energy, transportation, infrastructure and land use, as well as wastes and emissions into air and water. Transport of the raw materials, auxiliaries and wastes is included, transport and storage of the product are not included. Carbon Dioxide is the byproduct generated. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Values are taken principally from EFMA 2000 and Frischknecht 1999 (see report). Inventory refers to 1 kg 100% ammonia, liquid, at plant.	average of numbers for steam reforming (85%) and partial oxidation of heavy fuel oil (15%)	average of numbers for steam reforming (85%) and partial oxidation of heavy fuel oil (15%)
ReferenceFunction	CASNumber	7664-41-7	7664-41-7	7664-41-7	7664-41-7
TimePeriod	StartDate	2000-12	2000-12	2000-12	2000-12
TimePeriod	EndDate	2000-12	2000-12	2000-12	2000-12
TimePeriod	DataValidForEntirePeriod	1	1	1	1
TimePeriod	OtherPeriodText	Values based on reports from 1995 and 2000, and on literature with data from unknown date.	Values based on reports from 1995 and 2000, and on literature with data from unknown date.	Values based on reports from 1995 and 2000, and on literature with data from unknown date.	Values based on reports from 1995 and 2000, and on literature with data from unknown date.
Geography	Text	European average values	European average values	European average values	European average values
Technology	Text	mostly present state of the art technology used in european ammonia production plants	mostly present state of the art technology used in european ammonia production plants	mostly present state of the art technology used in european ammonia production plants	mostly present state of the art technology used in european ammonia production plants
Representativeness	Percent				
Representativeness	ProductionVolume	unknown	unknown	unknown	unknown
Representativeness	SamplingProcedure	see OtherPeriodText	see OtherPeriodText	see OtherPeriodText	see OtherPeriodText
Representativeness	Extrapolations	Transports based on standard distances of EcoInvent. Infrastructure: proxy module used (chemical plant, organics)	Transports based on standard distances of EcoInvent. Infrastructure: proxy module used (chemical plant, organics)	Transports based on standard distances of EcoInvent.	Transports based on standard distances of EcoInvent.
Representativeness	UncertaintyAdjustments	none	none	none	none

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12 Ammonium bicarbonate

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 Review: Heiko Kunst, TU Berlin

12.1 Introduction

Ammonium bicarbonate (NH_4HCO_3 , CAS-N° 1066-33-7) is a white powder with a faint odour of ammonia. It is soluble in water. The most important chemical and physical properties of ammonium bicarbonate are given in Tab. 12.1.

Synonyms for ammonium bicarbonate: acid ammonium carbonate, ammonium acid carbonate, ammonium hydrogen carbonate, carbonic acid, monoammonium salt.

Tab. 12.1 Chemical and physical properties of ammonium bicarbonate¹

Property	Value	Unit
Formula weight	79.06	
Specific gravity	1.586	
Solubility in water	11.9 (0° C) 59.2 (60° C)	g/100 mL g/100 mL
Density	1.586	g/cm ³

¹: Taken from Chemfinder (2003) and Weston (2000)

The following description of production technology and use of ammonium bicarbonate are summarised from Wostbrock (2000), Weston (2000) and Chemfinder (2003).

12.2 Reserves and Resources

Ammonium bicarbonate is produced basically from ammonia and carbon dioxide. Therefore, the resources available as well as the reserves are the same as for the production of these two chemicals, described in the corresponding chapter. The world annual production in 1997 was estimated at ca. 100'000 Tons, almost half of which was produced in the Western hemisphere and the remainder in Asia.

12.3 Production Technologies and Use

12.3.1 Production technologies for the production of ammonium bicarbonate

Ammonium bicarbonate is best produced in aqueous solution, be it continuously or batch. The process is relatively easy to control. The following equation describes the exothermic reaction forming ammonium bicarbonate:

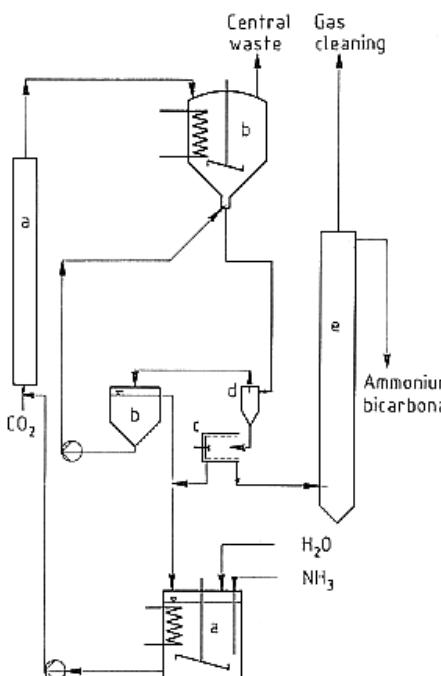


The heat of reaction must be removed, while the residence time, concentration, and temperature profile have to be controlled to yield large, easily separable crystals. The crystallization is the critical stage in the process.

The flow diagram of a continuous process is shown in Fig. 12.1. Ammonia is added to the mother liquor, which is kept cool, to achieve the desired NH_3 concentration of slightly above 10 wt %. Carbon dioxide is added and allowed to react in an absorption column. The resulting solution, which has been

warmed by the reaction, is cooled indirectly in a crystallizer. The crystal suspension is withdrawn, thickened in hydrocyclones, and passed to a centrifuge, where the solid is separated. This solid is pneumatically dried, cooled, and conditioned. The mother liquor is recycled.

The process variants of individual producers usually differ in the absorption/crystallization equipment, and this also results in different particle size distributions.



a) Gas absorption, b) Crystallization, c) Centrifugation, d) Thickening, e) Drying

Fig. 12.1 Production of ammonium bicarbonate (Taken from Wostbrock (2000): Fig. 15)

Ammonium bicarbonate is produced as both food and standard grade and the available products are normally very pure. Although purification is possible by sublimation at low temperatures, it is more economical to prepare the desired product directly by using ammonia and carbon dioxide of high purity.

12.3.2 Use

Ammonium bicarbonate is mainly used as an expanding agent for certain baked goods; it is also used in buffer solutions for neutralization of acids when additional anions are undesirable. Further uses include an ammoniation agent for the humic acid in turf, a nitrogen source for yeast cultures, and blowing agents for foam rubber and poly (vinyl chloride). Minor uses include smelling salts and formaldehyde binders in laminates. Ammonium hydrogencarbonate is also used in the production of textiles, ceramics, pigments, and leather.

12.4 System characterisation

This report corresponds to the module in the ecoinvent database for the **production of 1 kg ammonium bicarbonate, at plant, in Europe. All data are referred to 1 kg ammonium bicarbonate 100%.**

The system includes the process with the consumption of raw materials, energy, infrastructure and land use, as well as the generation of heat waste. Because of the lack of data on auxiliaries, emissions

and solid wastes, no values can be presented and therefore, the transportation and consumption of auxiliaries, the generation of emissions (other than heat waste) and solid wastes are not included.

Transportation of the raw materials is not included, since it is assumed that the ammonium bicarbonate plant produces also the most relevant raw materials or is very close to the corresponding plants. It also does not include transportation of the final product formaldehyde. There are no by-products generated in the production process.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage is also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers.

It is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

12.5 Ammonium bicarbonate production process

12.5.1 Data sources

Data regarding consumption of energy have been provided by a European manufacturing company for a previous study of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) in the early nineties. These numbers are confidential. Nevertheless, the company is probably not representative because of its size and operating conditions. This information is therefore taken only because of the lack of information in literature and is classified with very low reliability.

12.5.2 Raw materials and auxiliaries

The information provided by the manufacturing company does not include consumption of raw materials and auxiliaries. Therefore, for this study, consumption of raw materials is estimated basing on the stoichiometry of the reaction forming ammonium bicarbonate. For the calculations an operational efficiency of 95% is assumed, in concordance with Frischknecht et al. (2007).

Thus, for this study, the estimated values regarding consumption of raw materials for the production of 1 kg ammonium bicarbonate are 2.27 E-01 kg NH₃, 5.86 E-01 kg CO₂ and 2.40 E-01 kg H₂O.

12.5.3 Energy and transportation

For the production of 1 kg ammonium bicarbonate, the European manufacturing company consulted reports a consumption of 1.162 MJ electricity (medium voltage, production UCTE, at grid). Since electricity is reported in kWh in ecoinvent database, the necessary conversion is done according to Frischknecht et al. (2007). Thus, the value reported is 3.23 E-01 kWh per kg ammonium bicarbonate manufactured.

In regard to transportation, no information about distances is available in the examined data source. It is assumed that the production takes place in the same plant where ammonia is manufactured, or very close, so that the transportation of raw materials is not relevant.

12.5.4 Infrastructure and land use

There is no information available about infrastructure and land-use of ammonium bicarbonate plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about

this infrastructure module, see chapter 2.7 in part I of this report. Thus, for this study, the estimated value is 4.00 E-10 unit. kg⁻¹ chemical.

12.5.5 Emissions and Wastes

The information provided by the manufacturing company does not include generation of wastes or emissions to air and water.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. Thus, the value of waste-heat taken for this study is 1.162 MJ per kg ammonium bicarbonate manufactured.

12.6 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Data for consumption of energy of a very low reliability. Values for consumption of raw materials are estimations. This leads to high uncertainty scores.

Infrastructure data have also high uncertainty scores. Due to a complete lack of data, assumptions based on the very general module of an organic chemical plant are used.

Tab. 12.2 summarises the input and output data as well as the uncertainties used for the production of ammonium bicarbonate. The values are given for the production of 1 kg of 100% ammonium bicarbonate.

Tab. 12.2 Input- / Output-data for the production of ammonium bicarbonate (expressed per kg ammonium bicarbonate produced)

Explanation	Name	Location	Unit	ammonium bicarbonate, at plant	UncertaintyType	StandardDeviation5%	GeneralComment
	Location			RER o kg			
	InfrastructureProcess Unit						
Resources Input from Technosphere	Water, unspecified natural origin		m3	2.40E-1	1	1.21	(4,na,na,na,na,na); estimation on stoichiometry
	ammonia, liquid, at regional storehouse	RER	kg	2.27E-1	1	1.21	(4,na,na,na,na,na); estimation on stoichiometry
	carbon dioxide liquid, at plant	RER	kg	5.86E-1	1	1.21	(4,na,na,na,na,na); estimation on stoichiometry
	electricity, medium voltage, production	UCTE	kWh	3.23E-1	1	2.17	(3,5,4,5,5,5); data from a manufacturing company
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); estimation
Output air emission	ammonium bicarbonate, at plant	RER	kg	1			
	Heat, waste	RER	MJ	1.16E+0	1	2.17	(3,5,4,5,5,5); data from a manufacturing company

12.7 Cumulative Results and Interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

12.8 Conclusions

The inventory for ammonium bicarbonate is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if ammonium bicarbonate is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

12.9 EcoSpold Meta Information

ReferenceFunction	Name	ammonium bicarbonate, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	LocalName	Ammoniumbicarbonat, ab Werk
ReferenceFunction	Synonyms	Ammoniumhydrogencarbonat // Doppelkohlensaures Ammonium
ReferenceFunction	GeneralComment	Manufacturing process is considered with consumption of raw materials, energy, as well as infrastructure and land use. Transport of the raw materials is included. No by-product is generated in the process. Auxiliaries, solid wastes, emissions to air and water (excepting emission of waste-heat) are not included due to the lack of data. Transport and storage of the final product are not included. Transient or unstable operations are not considered, but the production during stable operation conditions. Inventory refers to 1 kg 100% ammonium bicarbonate. Data for consumption of energy have been provided by a manufacturer. Consumption of raw materials is estimated on stoichiometry assuming an efficiency of 95%. The literature source used is von Däniken et al. 1995.
ReferenceFunction	CASNumber	1066-33-7
TimePeriod	StartDate	1995-12
TimePeriod	EndDate	1995-12
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	Values based on data from the early 1990s.
Geography	Text	Data concerning energy have been provided by a European manufacturing company. No further information is available on the location and characteristics of this manufacturer. Therefore, the representativeness of these values for the European ammonium bicarbonate industry is unknown.
Technology	Text	unknown
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see geography
Representativeness	Extrapolations	Consumption of raw materials: estimation on stoichiometry (for an efficiency of 95%). Infrastructure: proxy module used (chemical plant, organics)
Representativeness	UncertaintyAdjustments	none

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13 Ammonium carbonate

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 Review: Heiko Kunst, TU Berlin

13.1 Introduction

Ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$, CAS-No. 506-87-6) – crystallizes according to Wostbrock et al. (2000) as flat, columnar, prismatic crystals resp. as elongated flakes. By melting at 316.2 K, ammonium carbonate is immediately decomposed into ammonium carbamate ($\text{NH}_4\text{CO}_2\text{NH}_2$) and ammonium sesquicarbonate ($(\text{NH}_4)_2\text{CO}_3 \cdot 2\text{NH}_4\text{HCO}_3 \cdot \text{H}_2\text{O}$). For this inventory the functional unit is 1 kg anhydrous, solid ammonium carbonate flakes. The most important chemical and physical properties of anhydrous ammonium carbonate used in this inventory are given in Tab. 13.1.

Tab. 13.1 Chemical and physical properties of ammonium carbonate (according to Weston (2000))

Property	Unit	Value	Remarks
Molecular weight	96.09	g mol^{-1}	
Melting point	43	°C	at normal pressure

13.2 Reserves and Resources of material

The production of ammonium carbonate is made out of ammonia and carbon dioxide (for more details see chapter 13.4). Therefore, all further discussion of resources equals to the discussion about ammonia (see ammonia in chapter 11 within this report here).

13.3 Use of material / product

According to Weston (2000) and Wostbrock et al. (2000), ammonium carbonate is used in a variety of different fields – e.g. it is the principal ingredient of smelting salts, in the manufacturing process of catalysts, as blowing agent for foam out of rubber or plastics, as additive in photographic developers, as well as in medicinal purposes or as leavening agent.

In 1997, the worldwide production capacity of ammonium carbonate was in the order of 7 kt.

13.4 Systems characterization

In the production process for ammonium carbonate the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of ammonium carbonate is not considered to be high. For this inventory the functional unit is 1 kg of anhydrous solid ammonium carbonate. As process location Europe (RER) is used.

According to Weston (2000) ammonium carbonate is produced by passing carbon dioxide into an absorption column containing aqueous ammonia solution and causing distillation. By condensation of ammonia, carbon dioxide and water vapors solid mass of crystals are formed.

13.5 Ammonium carbonate, at plant (Location: RER)

13.5.1 Process

This dataset includes a rough estimation of the production process for ammonium carbonate. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The mentioned production way for ammonium carbonate, can be summarized within the following overall stoichiometric reaction equation:



13.5.2 Resources

Energy

There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the ammonium carbonate production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 13.2.

Raw materials and Chemicals

According to the above shown final reaction equation - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of ammonium carbonate:

- carbon dioxide, CO_2 : 457.904 g (10.407 mol)
- ammonia, NH_3 : 353.835 g (20.814 mol)
- water, H_2O : 187.324 g (10.407 mol)

For the production a yield of 95% for the overall reaction is assumed. Therefore 482.004 g carbon dioxide, 372.458 g ammonia and 197.184 g water are considered as raw materials in this inventory. A summary of the values used is given in Tab. 13.2.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the ammonium carbonate production.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 \cdot 10^{-10}$ units per kg ammonium carbonate was included.

13.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg ammonium carbonate is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of ammonium carbonate. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input (carbon dioxide and ammonia).

This assumption leads to air emissions of 0.964 g carbon dioxide and 0.745 g ammonia.

Emissions to water

The remaining amount of unreacted raw materials was assumed to leave the production process with the wastewater. This assumption leads to a pollution of the waste water with 23.136 g carbon dioxide and 17.878 g of ammonia per kg product.

Further it was assumed that this wastewater is treated in an internal wastewater plant. For the ammonia within the waste water a removal efficiency for NH₄-N of 70% and for total N of 50% was assumed. The remaining emissions to water were considered as ammonium (NH₄) and nitrate (NO₃). The nitrogen emitted to air (N₂) and remaining in the sewage sludge was neglected. This assumptions lead to emissions of 5.679 g NH₄ and 13.04 g NO₃ per kg product in the treated water. The amount of CO₂ is assumed to be dissolved 100% in water in form of H₂CO₃. It leaves the WWTP unchanged. Therefore, 32.601 g H₂CO₃ are leaving. The values for TOC and DOC used in this inventory were calculated from this amount of H₂CO₃ in the treated waste water. For the calculation of the values for the worst case scenario TOC = DOC was used. COD and BOD are assumed to be zero. A summary of the values used in this inventory is given in Tab. 13.2.

Solid wastes

Solid wastes occurring during the production of ammonium carbonate were neglected in this inventory.

Tab. 13.2 Energy demand, Resource demand and emissions for the production of ammonium carbonate.

[per kg ammonium carbonate]			Remark
INPUTS			
carbon dioxide	kg	0.482	stoichiometric calc., 95% yield
ammonium	kg	0.372	stoichiometric calc., 95% yield
Water, unspecified	kg	0.197	stoichiometric calc., 95% yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m3	2.40E-02	estimation
Transport, by train	tkm	8.54E-02	standard distances & means
Transport, by lorry	tkm	4.27E-02	standard distances & means
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
ammonium, to air	kg	7.45E-04	estimated as 0.2% of input
carbon dioxide, fossil, to air	kg	9.64E-04	estimated as 0.2% of input
ammonium ion, to water	kg	5.68E-03	calculated from water emissions
nitrate, to water	kg	1.30E-02	calculated from water emissions
TOC, DOC	kg	6.31E-03	calculated from water emissions

13.6 Data quality considerations

Tab. 13.3 shows the data quality indicators for the inventory of ammonium carbonate production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the ammonium carbonate production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 13.9.

Tab. 13.3 Input / Output and uncertainty for the process “ammonium carbonate, at plant (RER)”

Explanation	Name	Location	Unit	ammonium carbonate, at plant	Uncertainty Type	Standard Deviations %	General Comment	
							Location	RER o kg
							Infrastructure	Process Unit
Resources Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant	
	Water, unspecified natural origin		m3	1.97E-04	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant	
	carbon dioxide, liquid, at plant	RER	kg	4.82E-01	1	1.21	(4,na,na,na,na); estimation based on process yield 90-99.8%	
	ammonia, liquid, at regional storehouse	RER	kg	3.72E-01	1	1.21	(4,na,na,na,na); estimation based on process yield 90-99.8%	
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant	
	transport, lorry 32t	RER	tkm	4.27E-02	1	2.09	(4,5,na,na,na); standard distances	
	transport, freight, rail	RER	tkm	8.54E-02	1	2.09	(4,5,na,na,na); standard distances	
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation	
	ammonium carbonate, at plant	RER	kg	1				
Output Air emission Water emission	Heat, waste		MJ	1.20E+00	1	1.88	(5.5,1,1,4,5); calculated from electricity input	
	Ammonia		kg	7.45E-04	1	2.32	(5,5,na,na,na,5); estimation	
	Carbon dioxide, fossil		kg	9.64E-04	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	Ammonium, ion		kg	5.68E-03	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	Nitrate		kg	1.30E-02	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	DOC, Dissolved Organic Carbon		kg	6.31E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	TOC, Total Organic Carbon		kg	6.31E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	

13.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

13.8 Conclusions

The inventory for ammonium carbonate is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if ammonium carbonate is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

13.9 EcoSpold Meta Information

ReferenceFunction	Name	ammonium carbonate, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Ammoniumcarbonat, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of solid, anhydrous ammonium carbonate flakes. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	506-87-6
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from carbon dioxide and ammonia with a process yield of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt. % of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	worldwide capacity (1997): 7 kt
Representativeness	SamplingProcedure	Process data based on stoichiometric
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	none

13.10 References

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14 Asbestos

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Last Changes:

2007

14.1 Introduction

Asbestos is a name for a variety of different, naturally occurring minerals. All of them are hydrated silicates that have a crystalline structure. Within them, two different types can be distinguished – amphibole (with a SiO₄ structure) and serpentine (with a layered silicate structure). More than 90% of the worldwide asbestos production is chrysotile - the only form of the latter type (Chissick (2000)). All further discussion here concerns only this type of asbestos minerals.

Chrysotile (CAS-No. 12001-29-5) has the chemical formula Mg₃[Si₂O₅](OH)₄. It is also called white asbestos. Like the other forms of asbestos, this material has a low thermal conductivity, is incombus-tible in air and can be separated into filaments. Due to their great tensile strength and thermal stability, asbestos fibres can even be spun into yarn (Chissick (2000)).

14.2 Resources and use of material

World leading producer of asbestos is Russia, followed by Canada, China, Brazil and Zimbabwe. In Europe, according to Euromines (2003), only in Greece asbestos is still mined. Concerning its use, some 3000 different uses are known – from paper and board, passing by asbestos cement pipes, roofing products and heat shields, to ‘fireproof’ textiles (Chissick (2000)).

14.3 Systems characterization

In the production process for asbestos in this study the main raw materials, an approximation of the production efforts (land-use, infrastructure, energy) and estimations for emissions based on similar processes are included. This module represents therefore only a rough estimation of the process requirements and should be used only when the impact of asbestos is not considered to be high.

As most economic way for the mining of chrysotile, open-pit mining has been proved. E.g. in Canada, about 95% of all asbestos ore is mined in open-pit operations by drilling and blasting operations (Chissick (2000)). This mining operation is followed by a cascade of different steps so that the asbestos fibres end up either in loose bags or pressure packed in 45-kg units. Within these different steps, the following main operation can be distinguished:

- Removal of waste rock and overburden and primary crushing;
- Secondary crushing, screening and drying;
- Shaking equipment for separation of freed fibres from the rock (repeated after further crushing and screening of the remaining material).

For this study, a production of asbestos by open-pit mining is assumed. Then the extracted material is separated from other minerals, followed by crushing and the shaking/aspiration process of the fibres. The functional unit for the inventory is 1 kg of fibrous asbestos, loose packed into multiwall paper bags. As process location Canada (CA) is used in this process.

14.4 Asbestos, crysotile type, at plant (Location: GLO)

Main data source for the asbestos production is Chissick (2000). As this mentioned source contains no quantitative information, process data from similar processes within this study are used as a first approximation for the asbestos production:

- *Mining*: the data for the mining operation are taken from limestone mining (Kellenberger et al. (2007)). As resource “crysotile, in ground” is used and due to a lack of respective information, an overall yield of 90% for crysotile is assumed in this project. All further information is taken 1:1 from limestone mining.
- *Crushing*: again, the data from limestone crushing are used as a first approximation. Therefore, the data are taken from the dataset “primary crushing of limestone” in Kellenberger et al. (2007).
- *Milling*: also therefore, data from the limestone production are used as first approximation.

Tab. 14.1 Input and output data for the production of 1 kg of asbestos (crysotile type)

Materials / Energy / Emissions		per kg asbestos	Remarks
Input			
chrysotile, in ground	kg	1.11E+00	assuming a yield of 90%
occupation, mineral extraction site	m2a	8.48E-05	estimation, based on limestone production
transformation, to mineral extraction site	m2	6.52E-06	dito
transformation, from forest	m2	6.52E-06	dito
recultivation, limestone mine	m2	6.52E-06	dito
water, well, in ground	m3	2.93E-05	dito
blasting	kg	7.73E-05	dito
diesel, burned in building machine	MJ	1.80E-02	dito
light fuel oil, low sulphur, burned in boiler 100 kw	MJ	3.59E-03	dito
heat, light fuel oil, at industrial furnace	MJ	8.98E-02	dito
mine, limestone	unit	5.25E-11	dito
industrial machine, heavy, unspecified, at plant	kg	2.31E-04	dito
conveyor belt, at plant	m	2.78E-08	dito
electricity, medium voltage, UCTE mix	kWh	3.25E-02	amount according to limestone production
Output			
waste, heat		1.17E-01	calculated from electricity input
particulates, > 10 um	kg	1.21E-04	estimation, based on limestone production
particulates, > 2.5 um and < 10 um	kg	4.78E-05	dito
particulates, < 2.5 um	kg	8.87E-06	dito

14.5 Data quality considerations

The uncertainty scores established according to the method used in this study (see Frischknecht et al. (2007)) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Here data from limestone production are used as an approximation for the asbestos production and therefore especially reliability, completeness and further technological correlation have high values, resulting in a high uncertainty for the whole process. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 14.8.

Tab. 14.2 Input / Output and uncertainty for the process “asbestos, crysotile type, at plant (GLO)”

Explanations	Name	Unit	asbestos, crysotile type, at plant	uncertaintyType StandardDeviation 95%	GeneralComment	
					Location	GLO
					InfrastructureProcess	0
Technosphere	Unit	kg			Unit	kg
	blasting	kg	7.73E-5	1	1.40	(4,3,1,3,3,5); approximation with data from lime production
	electricity, medium voltage, production UCTE, at grid	kWh	3.25E-2	1	1.40	(4,3,1,3,3,5); approximation with data from lime production
	diesel, burned in building machine	MJ	1.80E-2	1	1.40	(4,3,1,3,3,5); approximation with data from lime production
	light fuel oil, burned in boiler 100kW, non-modulating	MJ	3.59E-3	1	1.40	(4,3,1,3,3,5); approximation with data from lime production
	heat, light fuel oil, at industrial furnace 1MW	MJ	8.98E-2	1	1.40	(4,3,1,3,3,5); approximation with data from lime production
	industrial machine, heavy, unspecified, at plant	kg	2.31E-4	1	3.10	(4,3,1,3,3,5); approximation with data from lime production
	conveyor belt, at plant	m	2.78E-8	1	3.10	(4,3,1,3,3,5); approximation with data from lime production
	recultivation, limestone mine	m ²	6.52E-6	1	3.10	(4,3,1,3,3,5); approximation with data from lime production
	mine, limestone	unit	5.25E-11	1	3.10	(4,3,1,3,3,5); approximation with data from lime production
resources	Water, well, in ground	m ³	2.93E-5	1	1.40	(4,3,1,3,3,5); approximation with data from lime production
	Occupation, mineral extraction site	m ² a	8.48E-5	1	1.70	(4,3,1,3,3,5); approximation with data from lime production
	Transformation, to mineral extraction site	m ²	6.52E-6	1	2.20	(4,3,1,3,3,5); approximation with data from lime production
	Transformation, from forest	m ²	6.52E-6	1	2.20	(4,3,1,3,3,5); approximation with data from lime production
	Crysotile, in ground	kg	1.11E+0	1	1.40	(4,3,1,3,3,5); overall yield of 90% assumed
emission to air	Heat, waste	MJ	1.17E-1	1	1.40	(4,3,1,3,3,5); approximation with data from lime production
	Particulates, > 10 um	kg	1.12E-4	1	1.70	(4,3,1,3,3,5); approximation with data from lime production
	Particulates, > 2.5 um, and < 10um	kg	4.78E-5	1	2.20	(4,3,1,3,3,5); approximation with data from lime production
	Particulates, < 2.5 um	kg	8.87E-6	1	3.10	(4,3,1,3,3,5); approximation with data from lime production
Output	asbestos, crysotile type, at plant	kg	1.00E+0			

14.6 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

14.7 Conclusions

The inventory for asbestos is based on estimations and assumptions, starting with the dataset for limestone. The unit process raw data are meant to be used as background information if asbestos is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

14.8 EcoSpold Meta Information

ReferenceFunction	401	Name	asbestos, crysotile type, at plant
Geography	662	Location	GLO
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	402	IncludedProcesses	Raw materials, machineries and energy consumption for production, estimated emissions to air from production and infrastructure of the site (approximation). No water emissions.
ReferenceFunction	404	Amount	1
ReferenceFunction	490	LocalName	Asbest, Chrysotil-Typ, ab Werk
ReferenceFunction	491	Synonyms	
ReferenceFunction	492	GeneralComment	The functional unit represent 1 kg of asbestos. Quite a large uncertainty of the process data due to weak data on the production process.
ReferenceFunction	502	CASNumber	
TimePeriod	601	StartDate	2000
TimePeriod	602	EndDate	2000
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	date of published literature
Geography	663	Text	Data are used here as European average.
Technology	692	Text	Data approximated with data from lime mining, crushing and milling.
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	
Representativeness	725	SamplingProcedure	
Representativeness	726	Extrapolations	see technology
Representativeness	727	UncertaintyAdjustments	none

14.9 References

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15 Bitumen sealing

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15.1 Introduction

The following explications are based mainly on the respective chapter in Weibel & Stritz (1995).

Other (specific) types of bitumen sealing are included in the ecoinvent Database and reported on in Kellenberger et al. (2007)

According to Weibel & Stritz (1995), bitumen sealing tracks have to be protected against a natural ageing due to the fact that they are exposed to oxygen in air. Such a protection is usually made by covering the tracks with gravel. For the laying of the sealing tracks, two different techniques can be used – a casting technique and a welding technique.

In the ecoinvent project, a bitumen sealing with the technical properties described in Tab. 15.1 is taken as an example.

Tab. 15.1 Chemical and physical properties of bitumen sealing (according to information in Weibel & Stritz (1995))

Property	Unit	Value
Density	kg m ⁻³	1160
Heat conductivity	W mK ⁻¹	0.17
Vapour conductivity	Mg mhPa ⁻¹	2.8·10 ⁻⁵

15.2 Reserves and Resources of Material

The production of bitumen sealing is made out of different materials, whereof the main materials are based on oil (for more details see chapter 2.7). Therefore, all further discussion of resources can be found within the oil chapter in the respective report (Dones et al. (2007)).

15.3 Systems Characterization

The quantitative information for the production process of bitumen sealing is based mainly on information from one Swiss producer. They represent the situation of 1992 – since then several changes within the production line have taken place, but no respective numbers are available. According to experts, these new technologies feature ameliorations in the fields of energy consumption, emissions as well as the general working conditions. Thus, the module here represents only a first estimation of the process requirements and should be used accordingly.

For this inventory the functional unit is 1 kg of bitumen sealing. As process location Europe (RER) is used. A typical process flow scheme for the production of bitumen sealing is shown in Fig. 15.1.

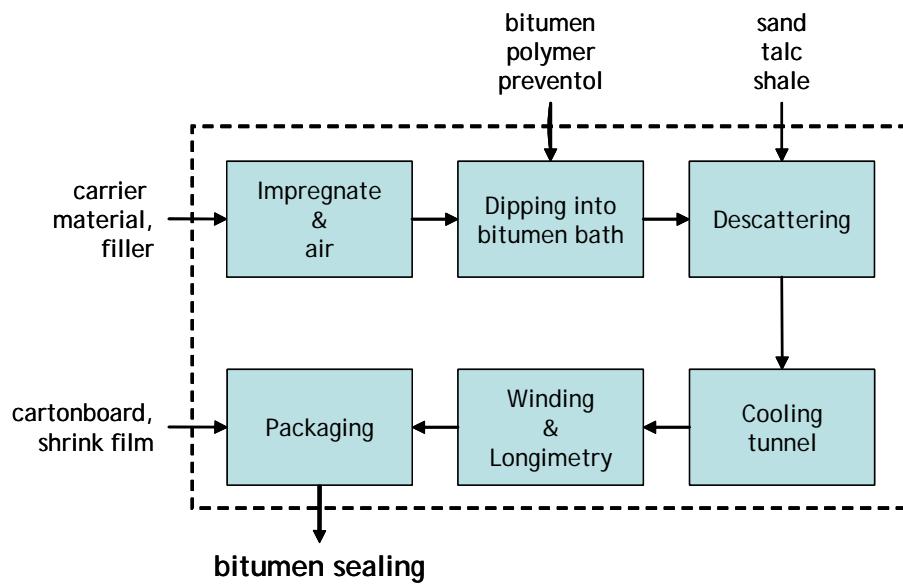


Fig. 15.1 Process chain for the production of bitumen sealing (according to Fig. 9.1 in Weibel & Stritz (1995))

According to Weibel & Stritz (1995), in a first step the carrier material (e.g. a polyethylene fleece) is preheated and aired (at a temperature of 165 – 195 °C) and in the next step it is dipped into the bitumen bath. This second step is situated in the so-called impregnate ladle at about 180°C. Further materials added in the beginning here are a filler as well as Preventol B2 (a herbicide). While the latter one avoids root penetration across the sealing, the first one enforces the weatherproof capacities, the mechanical stiffness as well as the flowing affinity in case of higher temperatures.

The third step – the descattering – aims in a better protection against UV radiation as well as against an intrusion of air oxygen. Therefore, talcum as well as silicon sand or shale is added. Before the sealing material can be winded, measured and packed, a cooling tunnel is passed to cool down the sealing track.

15.4 Bitumen sealing, at plant (Location: RER)

15.4.1 Resources

Raw Materials and Chemicals

According to Weibel & Stritz (1995), the production of 1 kg of bitumen sealing requires the materials summarized in Tab. 15.2. These values are based on the information from one Swiss producer and are valid for the production situation until 1993 (see also remarks in chapter 15.3). Due to a lack of more recent information, these data are nevertheless used within this study here.

Tab. 15.2 raw material and chemicals consumption for the production of 1 kg bitumen sealing (data from Weibel & Stritz (1995))

Input	Amount	Unit	Remarks
descattering material	6.00E-02	kg	shown as 80% talcum and 20% silica sand
bitumen	6.30E-01	kg	-
elastomer	7.00E-02	kg	shown as "polystyrene, general purpose"
filler	1.80E-01	kg	shown as "quicklime, milled, loose"
paper	2.31E-03	kg	shown as "paper, woodfree, uncoated"
preventol B2	8.00E-03	kg	shown as unspecified "chemicals, organic"
shrink material	2.49E-03	kg	shown as "packaging film, LDPE"
carrier	6.00E-02	kg	shown as "fleece"
packaging (cartonboard)	1.04E-02	kg	shown as "solid bleached board (SBB)"

Energy

According to Weibel & Stritz (1995), the production of 1 kg of bitumen sealing requires the different energy carriers summarized in the following table. These values are based on the information from one Swiss producer and are valuable for the production situation until 1993 (see also remarks in chapter 15.3). Due to a lack of more recent information, these data are nevertheless used within this study here.

Tab. 15.3 energy consumption for the production of 1 kg bitumen sealing (data from Weibel & Stritz (1995))

Input	Amount	Unit	Remarks
gas	9.30E-03	MJ	shown as "heat, natural gas, at industrial furnace >100kW"
oil	9.23E-01	MJ	shown as "heat, heavy fuel oil, at industrial furnace 1MW"
electricity	5.40E-02	MJ	shown as UCTE mix

Water use

In Weibel & Stritz (1995) is no information on the water consumption. For this study it is assumed, that the cooling tunnel uses water as heat transporting medium. Therefore, in order not to neglect the cooling water demand of the process, this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the bitumen sealing production.

For the process itself, it is assumed that no water is used.

Transport and Infrastructure

According to Weibel & Stritz (1995), the production of 1 kg of bitumen sealing is connected with the transport amounts summarized in Tab. 15.4. These values are based on the information from one Swiss producer and are valuable for the production situation until 1993 (see also remarks in chapter 15.3). Due to a lack of more recent information, these data are nevertheless used within this study here.

Tab. 15.4 transport efforts for the production of 1 kg bitumen sealing (data from Weibel & Stritz (1995))

Input	Amount	Unit	Remarks
transport on the road	3.23E-01	tkm	shown as "transport, lorry 32t"
transport on the rail	2.72E-01	tkm	shown as "transport, freight, rail"

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg bitumen sealing was included.

15.4.2 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 0.054 MJ per kg bitumen sealing is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air / water

In Weibel & Stritz (1995) no process specific emissions to air or to water are mentioned – only a reference to the emissions included in the fuels / materials is made. Therefore, in this study, no process specific emissions are assumed.

Solid wastes

According to Weibel & Stritz (1995), the production of 1 kg of bitumen sealing produces the different amounts of waste summarized in the following table. These values are based on the information from one Swiss producer and are valuable for the production situation until 1993 (see also remarks in chapter 15.3). Due to a lack of more recent information, these data are nevertheless used within this study here.

Tab. 15.5 waste amount of the production of 1 kg bitumen sealing (data from Weibel & Stritz (1995))

Input	Amount	Unit	Remarks
bitumen residues	3.77E-03	kg	shown as "disposal, bitumen, to sanitary landfill"
unspecified waste to landfill	9.54E-06	kg	shown as "disposal, municipal waste, to sanitary landfill"

15.5 Data quality considerations

Tab. 15.6 shows the data quality indicators for the inventory of bitumen sealing production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the bitumen sealing production has a quite high uncertainty, because they are out of date (representing the beginning of 90s) and based on a different geographical area (one Swiss company, used as representative for European average). A higher uncertainty exists for the cooling water demand. Due to missing data its value is based mainly on assumptions and approximations. Also for the infrastructure only an approximation was used because of missing data. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 15.8.

Tab. 15.6 Input / Output and uncertainty for the process “bitumen sealing, at plant (RER)”

Explanation	Name	Location	Unit	bitumen sealing, at plant		UncertaintyType	StandardDeviation95%	GeneralComment			
				RER 0 kg							
		Location	InfrastructureProcess								
		Unit	Unit								
Resources	Water, cooling, unspecified natural origin		m ³	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. Plant				
Input from Technosphere	malusil, at plant	RER	kg	4.80E-02	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	silica sand, at plant	CH	kg	1.20E-02	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	bitumen, at refinery	RER	kg	6.30E-01	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	polystyrene, general purpose, GPPS, at plant	RER	kg	7.00E-02	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	quickslime, milled, loose, at plant	CH	kg	1.80E-01	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	paper, woodfree, uncoated, at regional storage	RER	kg	2.31E-03	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	chemicals organic, at plant	GLO	kg	8.00E-03	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	packaging film, LDPE, at plant	RER	kg	2.49E-03	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	fleece, polyethylene, at plant	RER	kg	6.00E-02	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	solid bleached board, SBB, at plant	RER	kg	1.04E-02	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	heat, natural gas, at industrial furnace >100kW	RER	MJ	9.30E-03	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	9.23E-01	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.50E-02	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	transport, lorry 32t	RER	tkm	3.23E-01	1	2.12	(2,4,3,3,3,5); data from 1 Swiss company				
	transport, freight, rail	RER	tkm	2.72E-01	1	2.12	(2,4,3,3,3,5); data from 1 Swiss company				
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation				
	disposal, bitumen, 1.4% water, to sanitary landfill	CH	kg	3.77E-03	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
	disposal, municipal solid waste, 22.9% water, to municipal incineration	CH	kg	9.54E-06	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company				
Output	bitumen sealing, at plant	RER	kg	1							
Air emission	Heat, waste		MJ	5.40E-02	1	1.35	(2,4,3,3,3,5); calculated from electricity input				

15.6 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

15.7 Conclusions

An average European dataset for the production of bitumen sealing for the year 2000 is established. The dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on a former LCI report about construction materials. The dataset of bitumen sealing is based on information from one Swiss company and refers to the beginning of 1990s. The data are thus of a reasonable quality and can be used in quite a broad context.

15.8 EcoSpold Meta Information

ReferenceFunction	Name	bitumen sealing, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, energy consumption and waste amounts from a company. Infrastructure of the plant as an approximation.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Bitumendichtungsbahn, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represents 1 kg of bitumen sealing.
ReferenceFunction	CASNumber	
TimePeriod	StartDate	1992
TimePeriod	EndDate	1993
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	time to which data refer
Geography	Text	data from 1 Swiss company are used for the European average
Technology	Text	technology, used at the beginning of the 90s
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	Process data based on data from 1 Swiss company, used here as average data for European situation.
Representativeness	Extrapolations	see geography
Representativeness	UncertaintyAdjustments	none

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16 Borates, borax and boric acid

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Last changes:

2007

16.1 Introduction

Boron, the fifth element in the periodic table, does not occur in nature in its elemental form. Rather, boron combines with oxygen as a salt or ester of boric acid. There are more than 200 minerals that contain boric oxide but relatively few that are of commercial significance. In fact, three minerals represent almost 90% of the borates used by industry: tincal (a sodium borate), ulexite (a sodium–calcium borate) and colemanite (a calcium borate). Boron is according to Smith (2000) the fifth element in the periodic table and the only non-metallic element that is electron-deficient. It can be found in our earth crust at an average concentration of only about 10 ppm.

The mineral tincal ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is also called “natural borax” and is one of the two sodium borates with economic relevance. The other one is the mineral kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$). Here in this study, borax is synonym for the anhydrous borax form ($\text{Na}_2\text{B}_4\text{O}_7$, CAS-No. 1330-43-4), also called disodium tetraborate.

Calcium borates are besides sodium borates the most important sources of borates. According to Smith (2000), colemanite (CAS-No. 12291-65-5) is the most widely occurring calcium borate. It has the composition of $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ that can be written also as $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$.

Boric acid exists according to Smith (2000) in two different forms – in a trihydrate form as orthoboric acid (H_3BO_3 , CAS-No. 10043-35-3) or in a monohydrate form as metaboric acid (HBO_2 , CAS-No. 13460-50-9). As only the first mentioned form is of economic interest and importance, within this study boric acid is synonym for orthoboric acid. It crystallizes at room temperature as solid in form of odourless, white, waxy platelets. For this inventory the functional unit is 1 kg of boric acid (active substance). The inventory refers to technical grade anhydrous boric acid (99.9% boric acid). The most important chemical and physical properties of boric acid used in this inventory are given in Tab. 16.1. Synonyms for boric acid: trihydrate, orthoboric acid.

Tab. 16.1 Chemical and physical properties of orthoboric acid (according to Chemfinder (2002))

Property	Unit	Value	Remarks
Molecular weight	61.832	g mol^{-1}	
Boiling point	300	°C	at normal pressure
Melting point	171	°C	at normal pressure

16.2 Reserves and Resources of material

Large and therefore economic interesting amounts of boron containing minerals can be found only at few places over the whole world. Most of these sites have been volcanic active sites in the past. According to Smith (2000) are the Californian as well as the Turkish boron mines the most important ones worldwide. The production of boric acid is made from borate minerals and brines (Smith (2000)). As borate minerals, in Europe colemanite from Turkey is used while in the United States mainly sodium borate minerals (borax, kernite) are taken therefore.

16.3 Use of material / product

Most important customer for the boron companies is the glass industry. According to Lyday (2000), glass industry was in 2000 consuming in the United States 76% of all boron - Smith (2000) reports that in Europe about half of the boron is used by the glass industry. Other uses – all of them only of minor importance – are e.g. agricultural fertilizers, soaps and detergents.

According to Smith (2000), boric acid is used in about the same situations like boric oxides. In general, boric oxide are used largely in the glass and ceramic industry, while boric acid is more likely to be used e.g. as fire retardants, as fertilizer, as cleaning and bleaching agent or even as corrosion inhibitor.

The total boron production in 1999 is estimated to about 4.4 Mt – whereof the United States are production about 1.2 Mt and the Turkey estimated 1.4 Mt (Lyday (2000)). In 1982, according to Smith (2000), the worldwide production of boric oxides and acids was in the order of 950 kt. Thereof, more than half of it is from the United States and another about one third is from Turkey – the two main producing countries. More recent production numbers of boric acid were not available.

16.4 Systems characterization

The whole boron system in this study is interlinked according to Fig. 16.1.

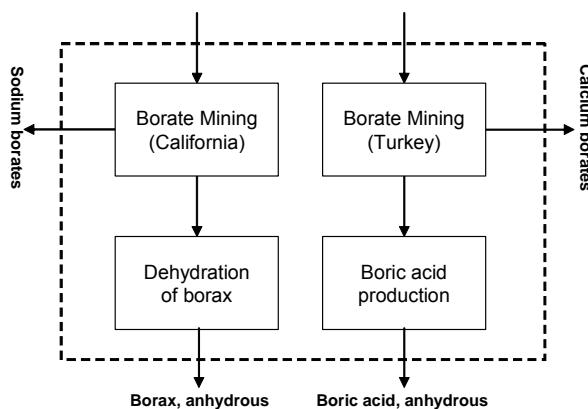


Fig. 16.1 The system of boron processes within this study

Therefore, in this study here four different modules are established – as there are:

- The extracted minerals: “Sodium borates, at plant (US)“ and “Calcium borates, at plant (TR)“
- The anhydrous borax module: “Borax, anhydrous, powder, at plant (GLO)“
- The boric acid module: “Boric acid, anhydrous, powder, at plant (RER)“

The two modules of extracted minerals are assumed to represent an open-pit mining extraction followed by a primary as well as a secondary crusher step (according to information in Smith (2000) and Azapagic & Clift (1999)). In this study, the raw material, the use of energy and auxiliaries as well as emissions to air and water are based on similar processes of other minerals. This module represents therefore only a rough estimation of the process requirements and should be used only when the impact of the different borates minerals is not considered to be high. For these inventories, the functional unit is 1 kg of sodium borates rsp. calcium borates. As process location – according with the reserves – the US (United States) is used for sodium borates and TR (Turkey) is used for calcium borates.

For the production process of the anhydrous borax module, an approximation of the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of boric acid is not considered to be high. For this inventory the functional unit is 1 kg of anhydrous borax. As process location GLO is used.

In the production process for boric acid the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of boric acid is not considered to be high. For this inventory the functional unit is 1 kg of solid boric acid. As process location Europe (RER) is used.

16.5 Sodium borates, at plant (Location: US)

16.5.1 Process

For this study, the sodium borate extraction of Rio Tinto Borax in Boron (California, USA) is taken as example where the extraction happens by open pits mining. According to Rio Tinto Borax (2001), the pit has a size of 1 x 1.5 miles (around 3.9 km²) and a depth of up to 700 feet. Mining activities extract about 3 Mio t of mine ore. The content of borax within the mined ore is not reported. Thereof, according to Lyday (2000), a production of 570 kt of boron was achieved. The mine is assumed to be used during 75 years.

All further process data for the mining activities are taken from the iron mining process (see Classen et al. (2007)). As a first approximation for the two above mentioned crushing steps, data from crushing and from milling (for the secondary crushing) from limestone are used in form of the dataset “primary crushing of limestone” and “milling of limestone” in Kellenberger et al. (2007). As there is no information available about the efficiency of the whole borate extraction chain, an overall yield of 80% is assumed here. All in all, this results in the input and output data shown in Tab. 16.2.

Tab. 16.2 Input and Output data for the production of 1 kg of sodium borates

Materials / Energy / Emissions		per kg sodium borates	Remarks
Input			
borax, in ground	kg	1.25E+00	Assumption: overall yield of 80%
water, well, in ground	m3	2.93E-05	estimation, based on crushing of limestone
occupation, mineral extraction site	m2a	7.06E-03	estimation, based on data from californian boron mine
transformation, to mineral extraction site	m2	9.42E-05	dito
transformation, from forest	m2	9.42E-05	dito
recultivation, iron mine	m2	9.42E-05	dito
blasting	kg	2.71E-04	estimation, based on iron ore extraction
diesel, burned in building machine	MJ	2.55E-02	dito
light fuel oil, burned in boiler 100kW, non-modulating	MJ	3.00E-03	estimation, based on limestone crushing & milling
electricity, medium voltage, UCTE mix	kWh	3.39E-02	estimation, based on extraction, crushing & milling
heat, light fuel oil, at industrial furnace	MJ	8.98E-02	estimation, based on limestone milling
mine, iron	unit	8.33E-13	estimation, based on iron ore extraction
industrial machine, heavy, unspecified, at plant	kg	2.31E-04	estimation, based on limestone crushing & milling
conveyor belt, at plant	m	2.78E-08	estimation, based on crushing of limestone
Output			
waste, heat		1.22E-01	calculated from electricity input
particulates, > 10 um	kg	1.45E-03	estimation, based on extraction & crushing
particulates, > 2.5 um and < 10 um	kg	1.31E-03	dito
particulates, < 2.5 um	kg	1.45E-04	dito

16.5.2 Data uncertainty and input data for database ecoinvent

The uncertainty scores established according to the method used in this study (see Frischknecht et al. (2007)) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Here data from iron mining and limestone crushing/milling are used as an approximation for the sodium borates production and therefore especially reliability, completeness and further technological correlation have high values, resulting in a high uncertainty for the whole process. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 16.11.

Tab. 16.3 Input data and uncertainty values for the dataset „sodium borates, at plant (US)“

Explanations	Name	Unit	sodium borates, at plant	uncertaintyType StandardDeviation 95%	GeneralComment	
					Location	US
					InfrastructureProcess	0
Technosphere	recultivation, iron mine blasting	m2	9.42E-5	1	3.80	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	electricity, medium voltage, production UCTE, at grid	kWh	2.71E-4	1	2.10	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	diesel, burned in building machine	MJ	3.39E-2	1	2.10	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	light fuel oil, burned in boiler 100kW, non-modulating	MJ	2.55E-2	1	2.10	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	heat, light fuel oil, at industrial furnace 1MW	MJ	3.00E-3	1	2.10	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	mine, iron	unit	8.98E-2	1	2.10	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	industrial machine, heavy, unspecified, at plant	kg	8.33E-13	1	3.80	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	conveyor belt, at plant	m	2.31E-4	1	3.80	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
			2.78E-8	1	3.80	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
resources	Water, well, in ground	m3	2.93E-5	1	2.10	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	Occupation, mineral extraction site	m2a	7.06E-3	1	2.30	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	Transformation, to mineral extraction site	m2	9.42E-5	1	2.80	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	Transformation, from forest	m2	9.42E-5	1	2.80	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	Borax, in ground	kg	1.25E+0	1	2.10	(4,3,1,3,5,5); estimated based on overall yield of 80%
emission to air	Heat, waste	MJ	1.22E-1	1	2.10	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	Particulates, > 10 um	kg	1.45E-3	1	2.30	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	Particulates, > 2.5 um, and < 10um	kg	1.31E-3	1	2.80	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
	Particulates, < 2.5 um	kg	1.45E-4	1	3.80	(4,3,1,3,5,5); approximation with data from iron mining & lime treatment
Output	sodium borates, at plant	kg	1.00E+0			

16.6 Calcium borates, at plant (Location: TR)

16.6.1 Process

The world biggest calcium borates production is in Turkey, situated in four different provinces in the western part of the country – south of the axe Istanbul – Ankara. As there is no quantitative information available about the Turkish mining activities, for this study, the data from sodium borates extraction of Rio Tinto Borax in Boron (California, USA) is taken as a first approximation. Like described in chapter 16.5, most of the values therefore are taken from the iron mining process, described in Classen et al. (2007) – only the land use (and transformation) numbers are specific for calcium borates.

For the further processing, similar to sodium borates, it is assumed for calcium borates that two mechanical steps follow - therefore, data from crushing and from milling of limestone are used in form of the dataset “primary crushing of limestone” and “milling of limestone” in Kellenberger et al. (2007). Again, due to a lack of further information, an overall yield of 80% is assumed for calcium borate. All in all, this results in the input and output data shown in Tab. 16.4.

Tab. 16.4 Input and Output data for the production of 1 kg of calcium borates

Materials / Energy / Emissions		per kg calcium borates	Remarks
Input			
colemanite, in ground	kg	1.25E+00	Assumption: overall yield of 80%
water, well, in ground	m3	2.93E-05	estimation, based on crushing of limestone
occupation, mineral extraction site	m2a	7.06E-03	estimation, based on data about sodium borates
transformation, to mineral extraction site	m2	9.42E-05	dito
transformation, from forest	m2	9.42E-05	dito
recultivation, iron mine	m2	9.42E-05	dito
blasting	kg	2.71E-04	estimation, based on iron ore extraction
diesel, burned in building machine	MJ	2.55E-02	dito
light fuel oil, burned in boiler 100kW, non-modulating	MJ	3.00E-03	estimation, based on limestone crushing & milling
electricity, medium voltage, UCTE mix	kWh	3.39E-02	estimation, based on extraction, crushing & milling
heat, light fuel oil, at industrial furnace	MJ	8.98E-02	estimation, based on limestone milling
mine, iron	unit	8.33E-13	estimation, based on iron ore extraction
industrial machine, heavy, unspecified, at plant	kg	2.31E-04	estimation, based on limestone crushing & milling
conveyor belt, at plant	m	2.78E-08	estimation, based on crushing of limestone
Output			
waste, heat		1.22E-01	calculated from electricity input
particulates, > 10 um	kg	1.45E-03	estimation, based on extraction & crushing
particulates, > 2.5 um and < 10 um	kg	1.31E-03	dito
particulates, < 2.5 um	kg	1.45E-04	dito

16.6.2 Data uncertainty and input data for database ecoinvent

The uncertainty scores established according to the method used in this study (see Frischknecht et al. (2007)) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Here data from iron mining and limestone crushing/milling are used as an approximation for the calcium borates production and therefore especially reliability, completeness and further technological correlation have high values, resulting in a high uncertainty for the whole process. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 16.11.

Tab. 16.5 Input data and uncertainty values for the dataset „calcium borates, at plant (TR)“

Explanations	Name	Unit	calcium borates, at plant	uncertaintyType	StandardDeviation		GeneralComment	
					95%			
					Location	TR		
Technosphere	InfrastructureProcess	Unit			InfrastructureProcess	0		
	recultivation, iron mine	m2	9.42E-5	1	3.80	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	blasting	kg	2.71E-4	1	2.10	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	electricity, medium voltage, production UCTE, at grid	kWh	3.39E-2	1	2.10	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	diesel, burned in building machine	MJ	2.55E-2	1	2.10	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	light fuel oil, burned in boiler 100kW, non-modulating	MJ	3.00E-3	1	2.10	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	heat, light fuel oil, at industrial furnace 1MW	MJ	8.98E-2	1	2.10	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	mine, iron	unit	8.33E-13	1	3.80	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	industrial machine, heavy, unspecified, at plant	kg	2.31E-4	1	3.80	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	conveyor belt, at plant	m	2.78E-8	1	3.80	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
resources	Water, well, in ground	m3	2.93E-5	1	2.10	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	Colemanite, in ground	kg	1.25E+00	1	2.10	(4.3,1,3,5,5); estimated overall yield of 80%		
	Occupation, mineral extraction site	m2a	7.06E-3	1	2.30	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	Transformation, to mineral extraction site	m2	9.42E-5	1	2.80	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	Transformation, from forest	m2	9.42E-5	1	2.80	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
emission to air	Heat, waste	MJ	1.22E-1	1	2.10	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	Particulates, > 10 um	kg	1.45E-3	1	2.30	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	Particulates, > 2.5 um, and < 10um	kg	1.31E-3	1	2.80	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
	Particulates, < 2.5 um	kg	1.45E-4	1	3.80	(4.3,1,3,5,5); approximation with data from iron mining & lime treatment		
Outputs	calcium borates, at plant	kg	1.00E+00					

16.7 Borax, anhydrous, at plant (Location: GLO)

16.7.1 Process

According to Sahin & Bulutcu (2002), anhydrous borax is produced by dehydration of hydrated sodium tetraborates (e.g. sodium borates like tincal or kernite) in three different ways – melting, azeotropic distillation or in a fluidized bed. In the first case – the most used technique in industry -, a rotary kiln is used in a first step for a partial dehydration before, in a second step, large fusion furnaces are used to eliminate completely all remaining water. By cooling down slowly, crystalline forms can be achieved as end result. This dataset here is assumed to represent this melting technique.

None of the examined sources contains quantitative information about the input of energy and the resulting emissions, therefore, the following assumptions are used for this dataset:

- **Material input:** Stoichiometric calculated amount of sodium borates, assuming a 50:50 split of tincal and kernite and a yield of 98% for the overall reaction. This means a total amount of 1705.01 g of sodium borates. For cooling it is assumed, as the cooling reaction is slow, that air is used and therefore, no water input (neither as cooling nor as process water) is included.
- **Energy input:** As a first approximation, the energy consumption of filament glass fibre production is used due to the fact that borates containing glasses are used for these fibres. According to European Commission (2000), the average input of energy to the furnace is for these fibres 11.2 to 23 GJ/t of produced fibres. Therefore, a value of 17 MJ/kg of borax is used here. It is assumed that it is 80% natural gas and 20% electricity.
- **Transport and infrastructure:** As there is no information about the transport amounts, it is assumed that the dehydration happens usually close to the mining site – therefore a transport of 50 km by lorry is assumed here. For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “glass production site” was used as a first approximation. For this module with a production capacity of 160'000 t per year and a plant life time of 50 years, an amount of 1.25×10^{-10} units per kg anhydrous borax was included.
- **Emissions to air and water:** The air emissions from the energy production are already included in the used energy datasets. Electricity consumption is shown – according to the methodology of the study – as waste heat to air. Concerning process emissions, the reaction produces water vapour, but no quantitative information is available and therefore, process emissions were neglected within this inventory.
- **Solids:** No information about solid wastes occurring during the production of anhydrous borax is available and therefore they were neglected in this inventory.

Tab. 16.6 Input and Output data for the production of 1 kg of anhydrous borax

[per kg borax, anhydrous]				Remark
INPUTS				
sodium borates	kg	1.705		stoichiometric calc., 98% yield
Electricity, medium voltage	kWh	0.9444444		estimation, from glass furnace
Natural gas, burned in industrial furnace >100kW	MJ	13.6		estimation, from glass furnace
transport by lorry	tkm	8.53E-02		based on assumed distance of 50 km
glass production site	unit	1.25E-10		approximation for infrastructure
OUTPUTS				
waste heat, to air	MJ	3.40E+00		calculated from electricity input

16.7.2 Data uncertainty and input data for database ecoinvent

The uncertainty scores established according to the method used in this study (see Frischknecht et al. (2007)) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Here data from iron mining and limestone crushing/milling are used as an approximation for the calcium borates production and therefore especially reliability, completeness and further technological correlation have high values, resulting in a high uncertainty for the whole process. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 16.11.

Tab. 16.7 Input data and uncertainty values for the dataset „borax, anhydrous, at plant (RER)“

Explanation	Name	Location	Unit	Borax, anhydrous, powder, at plant	uncertaintyType	standardDeviation95%	GeneralComment
				RER			
				0 kg			
Input from Technosphere	sodium borates, at plant	US	kg	1.71E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	electricity, medium voltage, production UCTE, at grid		kWh	9.44E-01			
	heat, natural gas, at industrial furnace >100kW		MJ	1.36E+01			
	glass production site		unit	1.25E-10		1	(5,5,1,1,4,5); estimated with data from a large chem. plant (4,5,1,3,5,4); estimation
	transport, lorry 32t		tkm	8.53E-02			
Output Air emission	Borax, anhydrous, powder, at plant	RER	kg	1			
	Heat, waste		MJ	3.40E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input

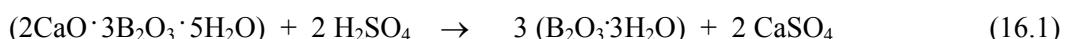
16.8 Boric acid, at plant (Location: RER)

16.8.1 Process

According to Smith (2000), the most modern boric acid plant works in California. There the crushed borate minerals are reacted with sulphuric acid at about 100°C. The solution is nearly saturated with sodium sulphate – thus, the liquid is filtered, removing boric acid as a solid. The produced sodium sulphate is partly returned to the reactor, while the remaining sodium sulphate is removed as solid esp. from the effluent stream. Also in Europe, sulphuric acid is used, there for the reaction with crushed colemanite minerals. As by-product in this case, gypsum (CaSO_4) is produced. In this study here, only the latter production way is taken into account.

The dataset established here includes a rough estimation of the production process for boric acid. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The examined production way for boric acid can be summarized within the following reaction equation:



16.8.2 Resources

Energy

There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1})

were used as approximation for the energy consumption of the boric acid production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 16.8.

Raw materials and Chemicals

According to the above shown reaction equation - the following stoichiometric inputs are needed (yield 100%) for the production of 1 kg of boric acid :

- Colemanite, $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$: 1870.839 g (5.391 mol)
- Sulphuric acid, H_2SO_4 : 1057.146 g (10.782 mol)

For the production a yield of 95% for the overall reaction out of borate minerals is used (see chapter 2.7). Therefore 1969.305 g calcium borates and 1113.069 g sulphuric acid are considered as raw materials in this inventory. A summary of the values used is given in Tab. 16.8.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the boric acid production.

No information about process water consumptions are available. According to the information in Smith (2000), it is assumed in this study that no additional process water input takes place – the water content originates from the input of sulphuric acid. Therefore in this study no input of process water is added to this dataset here.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials. This approximation is possible due to the fact that all Turkish boron mines are in the western part of the country.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg boric acid was included.

16.8.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. $1.2 \text{ MJ per kg boric acid}$ is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of boric acid. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input (without the calcium borates where no air emissions are assumed to occur). The assumption leads to air emissions of 2.226 g sulphuric acid.

Emissions to water

There is no input of process water. According to Smith (2000), the remaining liquid is recycled to the reactor and therefore no lost to the nature occurs.

By products and solid wastes

As by product, gypsum is produced within this process. Its amount is not taken further into account here as the process has the primary objective of boric acid production. No information about solid wastes occurring during the production of boric acid is available and therefore they were neglected in this inventory.

Tab. 16.8 Energy demand, Resource demand and emissions for the production of boric acid.

[per kg boric acid]			Remark
INPUTS			
calcium borates	kg	1.969	stoechiometric calc., 95% yield
sulphuric acid	kg	1.11E+00	stoechiometric calc., 95% yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m3	2.40E-02	estimation
transport by train	tkm	7.19E-01	calculated with standard distances
transport by lorry	tkm	1.20E-01	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
sulphuric acid, to air	kg	2.23E-03	estimated as 0.2% of input

16.8.4 Data quality considerations

Tab. 16.9 shows the data quality indicators for the inventory of boric acid production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the boric acid production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoechiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoechiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 16.11.

Tab. 16.9 Input / Output and uncertainty for the process “boric acid, at plant (RER)”

Explanation	Name	Location	Unit	<i>boric acid, anhydrous, powder, at plant</i>	uncertaintyType	standardDeviation35%	GeneralComment
				<i>RER 0 kg</i>			
				Location InfrastructureProcess Unit			
Resources Input from Technosphere	Water, cooling, unspecified natural origin	RER	m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	calcium borates, at plant		kg	1.97E+00	1	1.21	4,na,na,na,na,na); estimation based on process yield 90-99.8%
	sulphuric acid, liquid, at plant		kg	1.11E+00	1	1.21	4,na,na,na,na,na); estimation based on process yield 90-99.8%
	electricity, medium voltage, production UCTE, at grid		UCTE	kWh	3.33E-01	1	1.88
	heat, natural gas, at industrial furnace >100kW		RER	MJ	2.00E+00	1	1.88
	chemical plant, organics		RER	unit	4.00E-10	1	3.77
	transport, freight, rail		RER	tkm	7.19E-01	1	2.09
	transport, lorry 32t		RER	tkm	1.20E-01	1	2.09
Output Air emission	boric acid, anhydrous, powder, at plant	RER	kg	1			
	Heat, waste			MJ	1.20E+00	1	1.88
	Sulfate			kg	2.23E-03	1	2.32

16.9 Cumulative results and interpretation

Results of the cumulative inventory of the various substances can be downloaded from the database.

16.10 Conclusions

The inventories for the various B-containing substances are based on general literature (e.g. Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if one of these substances is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of these materials with other, alternative products.

16.11 EcoSpold Meta Information

ReferenceFunction	Name	sodium borates, at plant	calcium borates, at plant	Borax, anhydrous, powder, at plant	boric acid, anhydrous, powder, at plant
Geography	Location	US	RER	RER	RER
ReferenceFunction	InfrastructureProcess	0	0	0	0
ReferenceFunction	Unit	kg	kg	kg	kg
ReferenceFunction	IncludedProcesses	Raw materials, machineries and energy consumption for production, estimated emissions to air from production and infrastructure of the site (approximation). No water emissions.	Raw materials, machineries and energy consumption for production, estimated emissions to air from production and infrastructure of the site (approximation). No water emissions.	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air from production and energy demand as well as estimation of infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1	1	1	1
ReferenceFunction	LocalName	Natriumborate, ab Werk	Calciumborate, ab Werk	Borax, Pulver, wasserfrei, ab Werk	Borsäure, Pulver, wasserfrei, ab Werk
ReferenceFunction	Synonyms				
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of sodium borates. Large uncertainty of the process data due to weak data on the production process.	The functional unit represent 1 kg of calcium borate. Large uncertainty of the process data due to weak data on the production process.	The functional unit represent 1 kg of anhydrous borax powder. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.	The functional unit represent 1 kg of solid anhydrous boric acid (industrial grade). Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber		12291-65-5	1330-43-4	10043-35-3
TimePeriod	StartDate	2000	2000	2000	2000
TimePeriod	EndDate	2000	2000	2000	2000
TimePeriod	DataValidForEntirePeriod	1	1	1	1
TimePeriod	OtherPeriodText	date of published literature	date of published literature	date of published literature	date of published literature
Geography	Text	Data used represent conditions in California (USA).	Data used represent conditions in Turkey.	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Data approximated with data from iron mining as well as lime crushing and milling. Land-use data based on conditions for sodium borates mining in California (USA).	Data approximated with data from iron mining as well as lime crushing and milling. Land-use data based on conditions for sodium borates.	Production out of sodium borates by melting technology, using a rotary kiln and a subsequent fusion furnace. The overall process yield is assumed as 98%. Input amount bases on stoichiometric calculations. The energy consumption is estimated based on filament glass production in Europe.	Production from colemanite minerals (calcium borates) with the aid of sulphuric acid, having a process yield of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) were estimated.
Representativeness	Percent				
Representativeness	ProductionVolume				
Representativeness	SamplingProcedure			Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from other sector (glass production).	Process data based on information in just one literature source. Process emissions based on mass balance estimations.
Representativeness	Extrapolations	see technology	see technology		
Representativeness	UncertaintyAdjustments	none	none	none	none

16.12 References

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17 1-Butanol

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17.1 Introduction

1-Butanol ($C_4H_{10}O$, CAS-N° 71-36-3) is a colorless liquid with a strong, characteristic odour. The most important chemical and physical properties of 1-butanol are given in Tab. 17.1.

Synonyms for 1-butanol: n-butanol, butyl alcohol, n-butyl alcohol.

Tab. 17.1 Chemical and physical properties of 1-butanol (Taken from Chemfinder 2003)

Property	Value	Unit
Boiling point	117.6	°C
Melting point	-89	°C
Solubility in water	6.32	g/100mL
Vapor density	2.6	
Density	0.81	g/cm ³

The following description of production technology and use of butanol are summarised from Hahn (2000).

17.2 Reserves and Resources

1-butanol is produced basically from propylene. Therefore, the resources available as well as the reserves are the same as for the production of propylene, described the corresponding chapter. Both in the industrialized countries and worldwide, there is considerable excess capacity for the manufacture of 1-butanol (Hahn (2000)).

17.3 Production Technologies and Use

17.3.1 Production technologies for the production of 1-butanol

Of the many available processes for the preparation of 1-butanol, the following have achieved industrial importance: Propylene hydroformylation (oxo synthesis), Reppe synthesis and Crotonaldehyde hydrogenation.

Oxo Synthesis

This is the most important process for the manufacture of 1-butanol and 2-methyl-1-propanol. It consists on hydroformylation of propylene with subsequent hydrogenation of the aldehydes formed.

In the oxo reaction carbon monoxide and hydrogen are added to a carbon–carbon double bond in the liquid phase in the presence of catalysts (hydrocarbonyls or substituted hydrocarbonyls of Co, Rh, or Ru). In the first reaction step aldehydes are formed with one more C-atom than the original olefins. For olefins with more than two C-atoms, isomeric aldehyde mixtures are normally obtained. There are several variations of the hydroformylation process, the differences being in the reaction conditions (pressure, temperature) as well as the catalyst system used. Catalytic hydrogenation of the aldehydes

leads to the formation of the corresponding alcohols. As only primary alcohols can be obtained via the oxo synthesis, it is not possible to produce 2-butanol and 2-methyl-2-propanol by this process.

Reppe Process.

Another process to produce 1-butanol (and also 2-methyl-2-propanol) on a commercial scale is the carbonylation of propylene developed by Reppe. In this process, olefins, carbon monoxide, and water are made to react under pressure in the presence of a catalyst. The difference between this process and the classic Co-catalyzed hydroformylation is that at low temperature and low pressure alcohols are formed directly from the olefin. Nevertheless, the Reppe process has not been as successful as propylene hydroformylation with Co catalysts. This can be attributed to the more expensive process technology.

Hydrogenation of Crotonaldehyde

Until the mid 1950s the manufacture of 1-butanol based on acetaldehyde was the preferred process. Various gas- and liquid-phase processes have proved their value for the hydrogenation of crotonaldehyde to 1-butanol. Copper catalysts are particularly useful. With the development of the oxo synthesis, however, it has lost its importance and is no longer in use.

17.3.2 Use

1-Butanol is used principally in the field of surface coating. It is used either directly as a solvent for varnishes or it is converted into derivatives which then serve as solvents or monomer components. In the USA in particular, but also in the Federal Republic of Germany and Belgium, 1-butanol is used for the manufacture of butylamines. 1-Butanol has numerous applications also in the plastics and textile sector. It is used as a coagulation bath for spinning acrylic fibers and in the dyeing of poly(vinyl alcohol) fibers.

17.4 System characterisation

This report corresponds to the module in the ecoinvent database for the **production of 1 kg 1-butanol, at plant, in Europe**. For this study the production of 1-butanol by means of **oxo-synthese** is considered. **All data are referred to 1 kg 1-butanol 100%**.

The system includes the process with consumption of raw materials, energy, infrastructure and land use, as well as the generation of solid wastes and emissions to air and water. It also includes the transportation of the raw materials and wastes. Because of the lack of data on auxiliaries, no values can be presented and therefore, the transportation and consumption of auxiliaries are not included. The system also does not include transportation of the final product 1-butanol. There are no by-products generated in the production process.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage is also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers.

It is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

17.5 1-Butanol production process

17.5.1 Data sources

The data source for this study is von Däniken *et al.* (1995), a survey from the Swiss Agency for the Environment, Forests and Landscape (BUWAL). The module referring to 1-butanol bases on literature (Chauvel *et al.* (1986)¹⁹) for the consumption of energy and raw materials. For the emissions arising by the process the authors take, as an approximation, data from literature for the manufacturing of acetic acid by means of oxidation of liquid gas (Franklin (1989)²⁰) presented. The reason is that both processes are similar.

17.5.2 Raw materials and auxiliaries

According to von Däniken *et al.* (1995), 7.20 E-01 kg propylene, 7.80 E-01 m³ synthesis gas and 3.00 E-02 kg hydrogen are required for the manufacturing of 1 kg 1-butanol. Concerning the water consumption, Chauvel *et al.* (1986) reports an amount of 0.11 m³ cooling water and 0.001 m³ process water per kg 1-butanol produced.

17.5.3 Energy and transportation

The information on consumption of energy for the manufacturing of 1-butanol as presented in von Däniken *et al.* (1995), is shown in Tab. 17.2.

Tab. 17.2 Consumption of energy in the production of 1-butanol (Taken from von Däniken *et al.* (1995))

Input		(kg ⁻¹ 100% 1-butanol)
electricity	kWh	1.50 E-01
hardcoal	MJ	2.10 E+00
heavy fuel oil	MJ	1.30 E+00
light fuel oil	MJ	2.80 E-01
natural gas	MJ	3.20 E+00

¹: only gas for fuel. Synthesis gas used as raw material is not included.

In regard to transportation of raw materials and wastes, no information about distances is available in the examined data source. Therefore, for the raw materials, standard distances as defined in Frischknecht *et al.* (2007) are used: 100 km by lorry 32t and 600 km by train for propylene (standard values for transportation of ethylene are taken). For synthesis gas and hydrogen, standard numbers for transportation of gases are used: 50 km by lorry 32t and 100 km by train. For the transportation of the solid wastes it is assumed that they are sent to landfill and, again, standard distances are used: 10 km by lorry to disposal site. Additionally, it is assumed that this lorry has a capacity of 32 tonnes in order to facilitate the calculations. Transport amounts related to auxiliaries cannot be estimated since there are even no values for consumption of auxiliaries.

Tab. 17.3 summarises the total transport amounts for the production of 1 kg of 100% 1-butanol.

¹⁹ Chauvel *et al.* (1986): Chauvel *et al.* (1986) Precedes de petrochimie – caractéristiques techniques et économiques. Band II. Institut Français de Pétrole, Editions Technip.

²⁰ Franklin (1989): Franklin Associates, Ltd. (1989) The comparative energy and environmental impacts of soft drink delivery systems 1987 to 1995.

Tab. 17.3 Total transport amounts and means for the production of 1-butanol.

(tkm. kg ⁻¹ 100% 1-butanol)	lorry	train
raw material	7.22 E-02	4.35 E-01
auxiliaries	nd	nd
waste to disposal sites	7.20 E-06	0
Total transports	7.22 E-02	4.35 E-01

nd: no data available

17.5.4 Infrastructure and land use

There is no information available about infrastructure and land-use of butanol plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. Thus, for this study, the estimated value is 4.00 E-10 unit. kg⁻¹ chemical.

17.5.5 Emissions to air and water

von Däniken *et al.* (1995) presents values for specific process emissions. Emissions arised by the use of the different energy carriers are included in the correspondig modules and therefore are not further discussed here. Tab. 17.4 shows the information concerning emissions into air and into water, as presented in the mentioned source.

**Tab. 17.4 Process emissions to air and water from the production process of 1-butanol by means of the oxo-synthesis
(Taken from von Däniken *et al.* (1995))**

Process emissions ¹	Value (kg ⁻¹ 100% 1-butanol)	
Emissions to air		
Hydrocarbons	kg	3.91 E-03
Emissions to water		
BOD	kg	1.04 E-03
COD	kg	3.62 E-03
Suspended solids	kg	1.22 E-03
Hydrocarbons	kg	4.00 E-04

¹: Emissions corresponding to the use of energy carriers not included.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. Basing on this assumption and the necessary conversion from kWh to MJ is done according to Frischknecht *et al.* (2007). Thus, considering the energy input of 1.50 E-01 kWh. kg⁻¹ butanol, the value of waste-heat taken for this study is 5.40 E-01 MJ.kg⁻¹ butanol. Emission to air of unspecified hydrocarbons is reported as "Hydrocarbons, aliphatic, alkanes, unspecified" since this is most approximated module available in ecoinvent database.

17.5.6 Wastes

According to von Däniken et al. (1995), 7.20 E-04 kg solid wastes arise by the manufacturing of 1 kg 1-butanol. There is no further information about the substances included in this solid waste. For this study, solid waste is reported as “disposal, municipal solid waste, 22.9 %water, to sanitary landfill”, due to the above mentioned lack of information. This is considered the most appropriate among the different modules available in the database.

17.6 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Data presented in von Däniken et al. 1995 for consumption of energy and raw materials base on literature and might be updated. Values for emissions are estimations on a similar production process. The mentioned factors lead to higher uncertainty scores.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht et al. (2007) (transport) resp. the very general module of an organic chemical plant are used. This lack of representativeness is also reflected in the uncertainty scores.

Tab. 17.5 summarises the input and output data as well as the uncertainties used for the production of butanol. The values are given for the production of 1 kg of 100% butanol. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 17.9.

Tab. 17.5 Input- / Output-data for the production of 1-butanol (expressed per kg 100% 1-butanol produced)

Explanation	Name	Location	Unit	butanol, 1-, at plant	UncertaintyType	StandardDeviations95 %	GeneralComment	
							Location	InfrastructureProcess
								Unit
Resources	Water, cooling, unspecified natural origin		m3	1.10E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (Chauvet 1986)	
	Water, unspecified natural origin		m3	1.00E-3	1	1.34	(3,5,3,3,1,5); data from survey in literature (Chauvet 1986)	
	Gas, natural, in ground		Nm3	7.80E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (Chauvet 1986)	
Input from Technosphere	propylene, at plant	RER	kg	7.20E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	hydrogen, liquid, at plant	RER	kg	3.00E-2	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.50E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	hard coal, burned in industrial furnace 1-10MW	RER	MJ	2.10E+0	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	1.30E+0	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	heat, light fuel oil, at industrial furnace 1MW	RER	MJ	2.80E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	natural gas, burned in industrial furnace >100kW	RER	MJ	3.20E+0	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	transport, lorry 32t	RER	tkm	7.22E-2	1	2.05	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	transport, freight, rail	RER	tkm	4.35E-1	1	2.05	(4,na,na,na,na); standard distances	
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,na,na,na,na); standard distances	
	disposal, municipal solid waste, 22.9% water, to sanitary	CH	kg	7.20E-4	1	2.29	(4,1,5,3,5,4); estimation	
Output	butanol, 1-, at plant	RER	kg	1				
air emission	Heat, waste		MJ	5.40E-1	1	1.34	(3,5,3,3,1,5); calculated from electricity input	
	Hydrocarbons, aliphatic, alkanes, unspecified		kg	3.91E-3	1	2.35	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
water emission	BOD5, Biological Oxygen Demand		kg	1.04E-3	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	COD, Chemical Oxygen Demand		kg	3.62E-3	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	Suspended solids, unspecified		kg	1.22E-3	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	Hydrocarbons, unspecified		kg	4.00E-4	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	

17.7 Cumulative Results and Interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

17.8 Conclusions

An average European dataset for the production of butanol for the year 2000 is established. The dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on a re-

port covering the European industry, based on statistics from the first half of the 1990s. The data are thus of a reasonable quality and can be used in quite a broad context.

17.9 EcoSpold Meta Information

ReferenceFunction	401	Name	<i>butanol, 1-, at plant</i>
Geography	662	Location	RER
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	490	LocalName	Butanol, 1-, ab Werk
ReferenceFunction	491	Synonyms	Butylalkohol
ReferenceFunction	492	GeneralComment	The process considered is the production of 1-butanol by means of hydroformylation of propylene (oxo synthesis). Manufacturing process starting with propylene is considered, plus consumption of energy, infrastructure and land use, as well as generation of solid wastes and emissions into air and water. Transport of the raw materials and solid wastes is included. No by-product is generated in the process. Transportation and consumption of auxiliaries are not included due to the lack of data. Transport and storage of the final product are not included. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to landfill. Inventory refers to 1 kg 100% 1-butanol. In the source used (von Däniken et al. 1995) numbers for emissions are taken from the manufacturing of acetic acid, as an approximation.
ReferenceFunction	502	CASNumber	71-36-3
TimePeriod	601	StartDate	1995-12
TimePeriod	602	EndDate	1995-12
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	literature bases on data from the 1990s.
Geography	663	Text	In the literature source used, the numbers for emissions arisen by the production of butanol have been taken from the manufacture of acetic acid, as an approximation. It is not known how representative are these values for the European butanol industry
Technology	692	Text	unknown
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	unknown
Representativeness	725	SamplingProcedure	see geography
Representativeness	726	Extrapolations	Transports based on standard distances of Ecoinvent. Infrastructure: proxy module used (chemical plant, organics)
Representativeness	727	UncertaintyAdjustments	none

17.10 References

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18 Butyl acrylate

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18.1 Introduction

Butyl acrylate, also called n- butyl acrylate, ($C_7H_{12}O_2$, CAS-N° 141-32-2) is a colourless liquid. It is slightly soluble in water. The most important chemical and physical properties of butyl acrylate are given in Tab. 18.1.

Tab. 18.1 Chemical and physical properties of butyl acrylate (Taken from Chemfinder 2003)

Property	Value	Unit
Molecular weight	128.1706	
Boiling point	145	°C
Melting point	-64.6	°C
Solubility in water	<0.1 (at 20°C)	g/100mL
Density	0.894	g/cm ³

18.2 System characterization

This report corresponds to the module in the ecoinvent database for the **production of 1 butyl acrylate, at plant, in Europe**. For this study, and according to von Däniken *et al.* (1995), the production of butyl acrylate by means of the **esterification of acrylic acid with methanol** is considered. **All data are referred to 1 kg butyl acrylate 100%.**

The system includes the process with the consumption of raw materials, energy, infrastructure and land use as well as the generation of solid wastes and emissions to air and water. It also includes the transportation of the raw materials and wastes. Because of the lack of data on auxiliaries, no values can be presented and therefore, the transportation and consumption of auxiliaries are not included.

The system does not include transportation of the final product 1-butanol. There are no by-products generated in the production process.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage is also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers.

It is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

18.3 Butyl acrylate production process

18.3.1 Data sources

The data source for this study is von Däniken *et al.* (1995), a survey from the Swiss Agency for the Environment, Forests and Landscape (BUWAL). The module referring to butyl acrylate bases on literature (Chauvel *et al.* (1986)²¹) for the consumption of energy. For raw materials, it bases on a personal communication in 1992 of Akzo, a coating manufacturer. For the emissions arising by the process the authors take, as an approximation, data from literature for the manufacturing of dimethylterephthalate by means of the esterification of terephthalic acid with methanol (Franklin (1989)²²) presented. The reason is that both processes are similar.

18.3.2 Raw materials and auxiliaries

von Däniken *et al.* (1995) presents values for consumption of raw materials based on data provided by the manufacturing company Akzo, as mentioned above. According to this information source, 5.70 E-01 kg butanol and 5.90 E-01 kg acrylic acid are required for the manufacturing of 1 kg butyl acrylate.

Concerning the water consumption, Chauvel *et al.* (1986) reports an amount of 0.2m³ cooling water and 0.015 m³ process water per kg butyl acrylate produced.

18.3.3 Energy and transportation

The information regarding consumption of energy for the manufacturing of butyl acrylate as presented in von Däniken *et al.* (1995), is shown in Tab. 18.2. This source bases on literature data on consumption of electricity and thermal process energy. Basing on the latter, the authors calculate the consumption of different energy carriers.

Tab. 18.2 Consumption of energy in the production of butyl acrylate (Taken from von Däniken *et al.* (1995))

Input		(kg ⁻¹ 100% butyl acrylate)
electricity	kWh	3.00 E-02
hardcoal	MJ	5.13 E+00
heavy fuel oil	MJ	3.02 E+00
light fuel oil	MJ	6.80 E-01
natural gas	MJ	7.67 E+00

In regard to transportation of raw materials and wastes, no information about distances is available in the examined data source. Therefore, for the raw materials, standard distances as defined in Frischknecht *et al.* (2007) were used: 100 km by lorry 32t and 600 km by train. For the transportation of the solid wastes it is assumed that they are sent to landfill and, again, standard distances are used: 10 km by lorry to disposal site. Additionally, it is assumed that this lorry has a capacity of 32 tonnes in order to facilitate the calculations. Transport amounts related to auxiliaries cannot be estimated since there are no values even for consumption of auxiliaries.

²¹ Chauvel *et al.* (1986): Chauvel *et al.* (1986) Precedes de petrochimie – caractéristiques techniques et économiques. Band II. Institut Francais de Pétrole, Editions Technip.

²² Franklin (1989): Franklin Associates, Ltd. (1989) The comparative energy and environmental impacts of soft drink delivery systems 1987 to 1995.

Tab. 18.3 summarises the total transport amounts for the production of 1 kg of 100% butyl acrylate.

Tab. 18.3 Total transport amounts and means for the production of butyl acrylate.

(tkm. kg ⁻¹ 100% butyl acrylate)	lorry	train
raw material	1.16 E-01	6.96 E-01
auxiliaries	nd	nd
waste to disposal sites	2.80 E-06	0
Total transports	1.16 E-01	6.96 E-01

nd: no data available

18.3.4 Infrastructure and land use

There is no information available about infrastructure and land-use of butyl acrylate plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. Thus, for this study, the estimated value is 4.00 E-10 unit. kg⁻¹ chemical.

18.3.5 Emissions to air and water

von Däniken *et al.* (1995) presents values for specific process emissions. Emissions arised by the use of the different energy carriers are included in the correspondig modules and therefore are not further discussed here. Tab. 18.4 shows the information concerning process emissions into air and into water, as presented in the mentioned source.

Tab. 18.4 Process emissions to air and water from the production process of 1-butanol by means of the oxo-synthesis (Taken from von Däniken *et al.* (1995))

Process emissions ¹	Value (kg ⁻¹ 100% butyl acrylate)	
Emissions to air		
Hydrocarbons	kg	3.03 E-03
Dust	kg	2.30 E-04
Sulphuric dioxide	kg	1.95 E-03
Nitrogen oxides	kg	3.50 E-04
Emissions to water		
BOD	kg	1.90 E-04
COD	kg	8.87 E-04
Suspended solids	kg	2.60 E-04

¹: Emissions corresponding to the use of energy carriers are not included.

Dust is reported as Particulates and the value is splitted in the three fractions in use in ecoinvent database: Particulates, < 2.5 um; Particulates, > 2.5 um and < 10 um and Particulates, > 10 um. It is assumed that each fraction contributes with 33.3% to the total. Emission to air of unspecified hydrocarbons is reported as "Hydrocarbons, aliphatic, alkanes, unspecified" since this is most approximated module available in ecoinvent database.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. Basing on this assumption the necessary conversion from kWh to MJ is done according to Frischknecht et al. (2007). Thus, considering the energy input of 3.00 E-02 kWh, the value of waste-heat taken for this study is 1.08 E-01 MJ per kg butyl acrylate manufactured.

18.3.6 Wastes

According to von Däniken et al. (1995), 2.80 E-04 kg solid wastes arise by the manufacturing of 1 kg butyl acrylate. For this study, solid waste is reported as “disposal, municipal solid waste, 22.9 %water, to sanitary landfill”, due to lack of further information about the composition of the wastes mentioned. This is considered the most appropriate among the different modules available in the database.

18.4 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Data for consumption of energy base on literature and might be somewhat updated. Values for emissions are estimations on a similar production process. The mentioned factors lead to higher uncertainty scores. Data referring to consumption of raw materials have been provided by a manufacturing company, but since there is no information about this company and the background of these values, it is difficult to assess the uncertainty of the data.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht et al. (2007) (transport) resp. the very general module of an organic chemical plant are used. This lack of representativeness is also reflected in the uncertainty scores.

Tab. 18.5 summarises the input and output data as well as the uncertainties used for the production of butyl acrylate. The values are given for the production of 1 kg of 100% butyl acrylate. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 18.7.

Tab. 18.5 Input- / Output-data for the production of butyl acrylate (expressed per kg 100% butyl acrylate)

Explanation	Name	Location	Unit	butyl acrylate, at plant		UncertaintyType	StandardDeviation95%	GeneralComment
				RER	0 kg			
				InfrastructureProcess	Unit			
Resources	Water, cooling, unspecified natural origin		m3	2.00E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (Chauvet 1986)	
Input from Technosphere	Water, unspecified natural origin		m3	1.50E-2	1	1.34	(3,5,3,3,1,5); data from survey in literature (Chauvet 1986)	
	butanol, 1-, at plant	RER	kg	5.70E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	acrylic acid, at plant	RER	kg	5.90E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.00E-2	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	hard coal, burned in industrial furnace 1-10MW	RER	MJ	5.13E+0	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	3.02E+0	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	heat, light fuel oil, at industrial furnace 1MW	RER	MJ	6.80E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	natural gas, burned in industrial furnace >100kW	RER	MJ	7.67E+0	1	1.34	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	transport, lorry 32t	RER	tkm	1.16E-1	1	2.05	(4,na,na,na,na,na); standard distances	
waste	transport, freight, rail	RER	tkm	6.96E-1	1	2.05	(4,na,na,na,na,na); standard distances	
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); estimation	
	disposal, municipal solid waste, 22.9% water, to sanitary landfill	CH	kg	2.80E-4	1	2.29	(3,5,3,3,1,5); data from survey in literature (von Däniken et al. 1995)	
Output	butyl acrylate, at plant	RER	kg	1.00E+0				
air emission	Heat, waste		MJ	1.08E-1	1	1.34	(3,5,3,3,1,5); calculated from electricity input	
	Particulates, < 2.5 um		kg	7.67E-5	1	3.34	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	Particulates, > 2.5 um, and < 10um		kg	7.67E-5	1	2.35	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	Particulates, > 10 um		kg	7.67E-5	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	Sulfur dioxide		kg	1.95E-3	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	Nitrogen oxides		kg	3.50E-4	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	Hydrocarbons, aliphatic, alkanes, unspecified		kg	3.03E-3	1	2.35	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	BOD5, Biological Oxygen Demand		kg	1.90E-4	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	COD, Chemical Oxygen Demand		kg	8.87E-4	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	
	Suspended solids, unspecified		kg	2.60E-4	1	1.90	(3,5,3,3,4,5); data from survey in literature (von Däniken et al. 1995)	

18.5 Cumulative Results and Interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

18.6 Conclusions

An average European dataset for the production of butanol for the year 2000 is established. The dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on a report covering the European industry, based on statistics from the first half of the 1990s. The data are thus of a reasonable quality and can be used in quite a broad context.

18.7 EcoSpold Meta Information

ReferenceFunction	Name	butyl acrylate, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	The process considered is the production of butyl acrylat by means of the esterification of acrylic acid with metanol
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Butylacrylat, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The process considered is the production of butyl acrylat by means of the esterification of acrylic acid. Manufacturing process is considered with consumption of raw materials, energy, infrastructure and land use, as well as generation of solid wastes and emissions into air and water. Transport of the raw materials and solid wastes is included. No by-product is generated in the process. Transportation and consumption of auxiliaries are not included due to the lack of data. Transport and storage of the final product are not included. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to landfill. Inventory refers to 1 kg 100% butyl acrylate. In the source used (von Däniken et al. 1995) numbers for emissions are taken from the manufacturing of dimethylphthalate, as an approximation.
ReferenceFunction	CASNumber	141-32-2
TimePeriod	StartDate	1995-12
TimePeriod	EndDate	1995-12
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	literature bases on data from the 1990s.
Geography	Text	In the literature source used, the numbers for process emissions have been taken from the manufacture of dimethylphthalate, as an approximation. Data concerning consumption of raw materials and energy base on information provided by a coating manufacturing company (Akzo). It is not known how representative are these values for the European butyl acrylat industry
Technology	Text	unknown
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see geography
Representativeness	Extrapolations	Transports based on standard distances of Ecoinvent. Infrastructure: proxy module used (chemical plant, organics)
Representativeness	UncertaintyAdjustments	none

18.8 References

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19 Calcium carbide

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19.1 Introduction

Calcium carbide (CaC_2 , CAS-No. 75-20-7) is in its pure composition a colourless and odourless solid. But as the industrial grade is not a pure CaC_2 -solid, it is commonly known as a grey to brownish black solid that has an odour similar to phosphine. For this inventory the functional unit is 1 kg of sold industrial grade calcium carbide. The most important chemical and physical properties of calcium carbide used in this inventory are given in Tab. 19.1.

Synonyms for calcium carbide: -

Tab. 19.1 Chemical and physical properties of calcium carbide (according to Langhammer (2000))

Property	Unit	Value	Remarks
Molecular weight	g mol^{-1}	64.10	
Melting point	$^{\circ}\text{C}$	2160	at normal pressure
Decomposition temperature	$^{\circ}\text{C}$	2500	at normal pressure

According to Langhammer (2000), four different modification of calcium carbide are known – whereof phase I (tetragonal, stable from 25 to 440°C) is the mainly used commercial form.

19.2 Reserves and Resources of material

The production of calcium carbide is made out of quicklime and carbonaceous materials like e.g. coke or anthracite by using an electrothermic furnace. Therefore, all further discussion of resources can be found within the respective chapter about the limestone chain (Kellenberger et al. (2007)) resp. about coal (Dones et al. (2007)), showing information for coke and anthracite.

19.3 Use of material / product

According to Langhammer (2000), calcium carbide is used in three different cases: the production of acetylene (widely used as welding gas), the production of cyanamide (a fertilizer) and third, in the iron and steel industry as a desulphurization agent. This latter application is getting more and more important – as calcium carbide allows reducing the sulphur content in the steel melt from around 0.2% to 0.001%. In 1997, around 100 kt of calcium carbide were used in the European iron and steel industry.

Concerning its production, calcium carbide was at its top in the 60s, when the world production was in the order of 10 Mt. Since then, the annual amount declined steadily – reaching around 4.9 Mt in 1990. Besides the total production amount, also the main producing area changed within these 30 years. While in the 60s Western Europe was the biggest producer (accounting for almost one third of the total production), Asia and Africa have taken over this position in 1990, being responsible together for 43% of the total production.

19.4 Systems characterization

In the production process for calcium carbide the main raw materials, an approximation of the production energy and estimations for the emissions to air are included. This module represents therefore rather a rough estimation of the process requirements and should be used only for processes where the impact of calcium carbide is not considered to be high.

The whole process is operated within a furnace. No further steps are needed. For this inventory the functional unit is 1 kg of solid industrial-grade calcium carbide (80% calcium carbide in calcium oxide, CaO). As process location Europe (RER) is used.

19.5 Calcium carbide, at plant (Location: RER)

19.5.1 Process

The overall reaction for the production of calcium carbide can be formulated as follows:



The whole reaction is very strongly endothermic and therefore, the reaction energy has to be brought in from external energy sources. Thus, carbonaceous material is melted with CaO in a short electro-thermic shaft furnace. According to Langhammer (2000) this reaction has a economic sufficient reaction rate only at temperatures above 1600°C – while at temperatures above 2000°C undesirable side reactions get more and more important. Therefore, most furnaces operate nowadays at temperatures between 1800 and 2100°C, resulting in the production of technical-grade calcium carbide (80% purity).

For this study, a modern large calcium carbide furnace with traditional self-baking Söderberg electrodes is assumed.

19.5.2 Resources

According to Langhammer (2000), such a modern calcium carbide furnace requires per tonne calcium carbide 950 kg lime (94% CaO), 550 kg coke (dry, 10% fly ash) as well as 20 kg electrode materials. The energy demand for this process is in the order of 3'100 kWh electricity. Based on this information, the resources and the energy consumption can be established for the dataset of calcium carbide within this study here.

Energy

For the electricity consumption, the above mentioned amount of 3.1 kWh per kg calcium carbide is used. The amount is shown as average European electricity, using the UCTE-mix. A summary of the values used is given in Tab. 19.2.

Raw materials and Chemicals

According to the above listed amounts, an input of 0.55 kg coke and 0.893 kg CaO (94% of 0.95 kg lime, according to the indication in Langhammer (2000)) is used per kg of produced calcium carbide. For the electrode material (0.02 kg per kg produced CaC₂), coke is used as a first approximation within this study. A summary of the values used is given in Tab. 19.2.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the calcium carbide production.

It is assumed that no process water is used within the production of calcium carbide.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. As a first approximation, the infrastructure of the glass production (dataset “glass production site (RER)”) is used here – due to the fact that this process here uses a furnace similar to the glass production. For this module with a production capacity of 160'000 t per year and a plant life time of 50 years, an amount of $1.25 * 10^{-10}$ units per kg calcium carbide was included.

19.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 3.1 kWh per kg calcium carbide is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

According to Langhammer (2000), the furnace gas have an average composition of 85 vol-% CO, 10.5% H₂, 1.5% CO₂, 0.5% CH₄ and 2.5% N₂. About the amount of furnace gas emissions, no information is given in this source – therefore, its amount is calculated by using mass balance principles for the amount of carbon monoxide. For the carbon monoxide emissions, the reaction equation above shows, that per mol of calcium carbide, 1 mol of carbon monoxide is produced. This leads for the production of 1 kg of calcium carbide to an emission of 436.817 g carbon monoxide (15.6 mol). For this study – as a first approximation – the 85 vol-% CO are equal to 436.82 g or 0.411 m³. This leads to the following further emissions: 3.880 g H₂, 12.192 g CO₂, 1.480 g CH₄ and 12.854 g N₂. In accordance with the methodology of the study, nitrogen is not included into the dataset.

Emissions to water

Water is used only in the form of cooling water within this production process. Therefore, no water emissions are taken into account in this study here.

Solid wastes

Solid wastes occurring during the production of calcium carbide were neglected in this inventory.

Tab. 19.2 Energy demand, Resource demand and emissions for the production of calcium carbide.

[per kg calcium carbide]			Remark
INPUTS			
coke	kg	0.550	according to Langhammer 2000
CaO (quicklime)	kg	0.893	according to Langhammer 2000
electrode material (coke)	kg	0.020	according to Langhammer 2000
Electricity, medium voltage	kWh	3.1	according to Langhammer 2000
Water, cooling, unspecified	m3	2.40E-02	estimation
transport by train	tkm	8.78E-01	standard distances
transport by lorry, 32t	tkm	1.46E-01	standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.12E+01	calculated from electricity input
carbon monoxide, fossil, to air	kg	4.37E-01	according to Langhammer 2000 & mass balance
carbon dioxide, fossil, to air	kg	1.22E-02	calculated from CO emissions
hydrogen, to air	kg	3.88E-03	calculated from CO emissions
nitrogen, to air	kg	1.29E-02	calculated from CO emissions
methane, fossil, to air	kg	1.48E-03	calculated from CO emissions

19.6 Data quality considerations

Tab. 19.3 shows the data quality indicators for the inventory of calcium carbide production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the calcium carbide production has quite a high uncertainty, because only few data (input of material and energy) of the production processes were available. The highest uncertainties exist for the emissions to air. Due to missing information these values are based on an approximation, passing by mass balance calculations. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Also for the infrastructure only an approximation was used because of missing data.

Additionally, the most important fields of the ecospold meta information from those datasets are listed in chapter 19.9.

Tab. 19.3 Input / Output and uncertainty for the process “calcium carbide, at plant (RER)”

Explanation	Name	Location	Unit	calcium carbide, technical grade, at plant		uncertainty Type	standardDeviation95%	GeneralComment	
				TR	O				
				kg					
Resource Input from Technosphere	Water, cooling, unspecified natural origin quicklime, milled, loose, at plant	CH	m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	hard coal coke, at plant		kg	8.93E-01	1	1.21	4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.10E+00	1	1.88	4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	transport, freight, rail	RER	tkm	8.78E-01	1	2.09	(4,5,1,3,5,4); estimation		
	transport, lorry 32t	RER	tkm	1.46E-01	1	2.09	(4,5,na,na,na,na); standard distances		
Output Air emission	calcium carbide, technical grade, at plant	TR	kg	1					
	Heat, waste		MJ	1.12E+01	1	1.88	(5,5,1,1,4,5); calculated from electricity input		
	Carbon dioxide, fossil		kg	1.22E-02	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Carbon monoxide, fossil		kg	4.37E-01	1	5.63	(5,5,na,na,na,5); estimation		
	Hydrogen		kg	3.88E-03	1	2.32	(5,5,na,na,na,5); estimation		
	Methane, fossil		kg	1.48E-03	1	2.32	(5,5,na,na,na,5); estimation		

19.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

19.8 Conclusions

The inventory for calcium carbide is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if calcium carbide is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

19.9 Ecospold Meta Information

ReferenceFunction	Name	calcium carbide, technical grade, at plant
Geography	Location	TR
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air from production and energy demand as well as estimation of infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Calciumcarbid,
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of solid industrial grade calcium carbide. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	75-20-7
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from coke and quicklime in a furnace with self-baking Söderberg electrodes (assumed to be coke as well). Inventory bases on information from literature. The emissions to air are calculated according to mass balance, while the composition is from literature.
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on information in just one literature source. Process emissions based on mass balance estimations.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

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20 Carbon black

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Last Changes:

2006

20.1 Introduction

In the production of printing colors, carbon black or soot is used as the pigment in the black color. In fact, carbon black is according to Dannenberg & Paquin (2000) a generic term for an important family of products used mainly in the rubber industry. Carbon black is a very fine powder, having a high surface area and being composed mainly out of carbon. For this inventory here the functional unit is 1 kg solid carbon black.

20.2 Resources and use of material

From the worldwide carbon black production the rubber tire industry is the most important consumer with about 70% of the world production. Another 20% are consumed for other rubber products than tires – and only the remaining 10% are non-rubber applications, like e.g. the use of black pigments for printing colors.

The worldwide production capacity of carbon black was in 1996 around 8 Mt (Voll & Kleinschmit (2002)). Thereof, North America represents around 1.8 Mt, Western Europe about 1.3 Mt, South East Asia and Australia around 2.6 Mt and Eastern Europe including Russia 1.5 Mt. Within Western Europe, most important producers are Germany (277 kt capacity) and France (280 kt).

20.3 Systems characterization

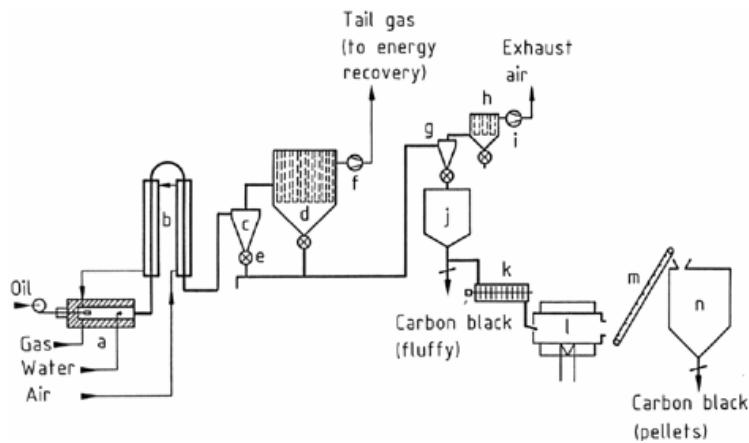


Fig. 20.1 Overview of oil-furnace production process for black carbon (Fig. 56 out of Voll & Kleinschmit (2002) – with Furnace black reactor [a], Heat exchanger [b], cyclone [c], Bag filter [d], Carbon black outlet to pneumatic conveying system [e], Tail gas blower [f], Collector [g], Exhaust air filter [h], Blower for the pneumatic conveying air [i], Fluffy black storage tank [j], Pelletizer [k], Dryer drum [l], Conveying belt [m] and storage tank for carbon black pellets [n])

The most important production process used nowadays is the oil-furnace process – other processes like e.g. thermal or acetylene carbon black processes are only of minor interests and therefore not further examined within this study here. The examined oil-furnace process is, according to Voll & Kleinschmit (2002) and Dannenberg & Paquin (2000) a partial combustion process of liquid aromatic residual hydrocarbons. Fig. 20.1 shows a schematic flow diagram of this production process.

The principle here is to atomize the feedstock into the reactor, where it is decomposed into carbon black and hydrogen due to the fact that the oxygen available is not sufficient for a combustion of all this input. The reactor temperature is in the order of 1200 to 1900 °C, achieved through the combustion of natural gas and of the unreacted feedstock. After the decomposition, a fast quenching has to be done to avoid the loss by reaction of carbon black with carbon dioxide and water. The further processing consists mainly of drying and separation from other substances like e.g. tail gases through a filter system. For this inventory the functional unit is 1 kg of solid carbon black. As process location Europe (RER) is used.

20.4 Carbon black, at plant (Location: RER)

For the carbon black production, Voll & Kleinschmit (2002), Dannenberg & Paquin (2000) and Frischknecht et al. (1996) are used as main data sources. The latter one is based mainly on data from two Dutch carbon black production sites, described in Zevenhoven-Onderwater & Matthijsen (1992).

According to Voll & Kleinschmit (2002) the yield of a carbon black furnace is in the order of 40 to 65% depending also on the form of carbon black. For this study, a yield of 65% is used.

Tab. 20.1 shows the reported input and output values from the different sources (Dannenberg & Paquin (2000) contains no quantitative information) as well as the values used in this study.

Tab. 20.1 Input and output data for the production of 1 kg of carbon black

		Frisch-knecht 1996	Voll 2002, type A ¹	Voll 2002, type B ¹	This study	Remarks
Input						
air	m3		4.86	5.40	5.13	not included into input data
natural gas	m3		0.24	0.29	0.27	as heat, from industrial furnace
Heavy fuel oil	kg	1.10E-02			-	
crude oil	kg	1	1.66	2.00	1.81	Assuming a yield of 65%
Output						
<i>Emissions to air</i>						
waste heat	MJ				5.18E+01	59% of energy content of input
moisture	kg		(25 - 40%)		-	
nitrogen	kg		(40 - 50%)		-	Tail gas flow is used as input into the internal energy production unit and incinerated.
carbon dioxide, fossile	kg		(3 - 5%)		-	
carbon monoxide, fossile	kg		(5 - 10%)		-	
hydrogen	kg		(5 - 10%)		-	
SOx from process	kg	0.0031			3.30E-03	total of combustion and process emissions
SOx from combustion	kg	2.00E-04				
NOx from process	kg	0.001			1.05E-03	total of combustion and process emissions
NOx from combustion	kg	5.00E-05				
carbon black, from process	kg	0.001			1.00E-03	additional process emission, reported as PM2.5
PAH from process	kg	1.00E-06			1.00E-06	additional process emission
carbon dioxide, fossile	kg				1.97E+00	calculated from mass balance
carbon monoxide, fossile	kg				8.30E-04	worste case, according to legal limits
<i>Emissions to water</i>						
Oil and grease, total	kg	2.40E-05			-	no water use within process
nitrogen, total	kg	1.30E-05			-	no water use within process

¹ A: Semireinforcing Carbon Black, B: Reinforcing Carbon Black

The values for this study are established thereby according to the following argumentation:

- *Input:* An average value from the two different types of carbon black reported in Voll & Kleinschmit (2002) is used for the input of natural gas (reported as “heat, from industrial furnace”). The feedstock input (as crude oil) is calculated from the assumed yield of 65% and a C-content of 85% for the crude oil. Due to a lack of more précis information, the dataset “crude oil, at production on-shore (RME)” is used for the complete input amount. In accordance with the general methodology of this study, the input of air is not further taken into account.
- *Water:* It is assumed in this study that this process has no water consumption – nor for the process nor for cooling systems – instead the cooling medium used here is air. Thus, no emissions into water are reported in this dataset.
- *Waste heat:* According to Dannenberg & Paquin (2000), 59% of the energy input are leaving the plant in form of waste heat emissions – thus in this study, 59% of the input energy amount of gas and oil is reported as “waste heat, to air”.
- *Emissions into air:* The tail gas, that leaves the process, has according to Voll & Kleinschmit (2002) an average composition of 35 vol-% water, 45% nitrogen, 5% carbon dioxide, 7.5% carbon monoxide as well as 7.5% hydrogen. There is no information about the amount (kg or m³) of tail gas that is produced per kg of carbon black. According to the different references used here, the tail gas is used internally for energy production. By this incineration process, all CO should theoretically be transformed into CO₂ (by a complete combustion process), while parts of the nitrogen are transformed into NO_x. Due to a lack of actual information about the various emissions, the following values are used here:
 - **NO_x & SO₂:** sum of values reported in Frischknecht et al. (1996) are used – representing the emissions from the process as well as those from the internal energy plant;
 - **CO:** According to Zevenhoven-Onderwater & Matthijsen (1992), the limitation for CO in the waste air stream is about 100 mg/m³, resulting in a emission of 0.83 g/kg carbon black¹;
 - **CO₂:** Out of the mass balance (assuming a C-content of 85% in the crude oil), a total CO₂ emission of 1.97 kg/kg carbon black can be calculated;
 - **Further emissions:** values from Frischknecht et al. (1996) are used.
- *Infrastructure and Transport:* Due to a lack of specific data, for the input of crude oil a transport distance of 500 km by lorry is assumed, and for the infrastructure the dataset "chemical plant, organics" is used.

20.5 Data quality considerations

The uncertainty scores established according to the method used in this study (see Frischknecht et al. (2007)) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. The material/energy data are based on information from literature, while the emission values are based on information from two Dutch plants. For the transports and the infrastructure, estimations are used and therefore the uncertainty is higher. Additionally, the most important fields of the ecoinvent meta information from those datasets are listed in chapter 20.8.

¹ A tail gas stream of 8.3 dm³/kg of carbon black produced is calculated, based on mass balance (assuming a C content of 85% in the crude oil used).

Tab. 20.2 Input / Output and uncertainty for the process “carbon black, powder, at plant (RER)”

Explanation	Name	Location	Unit	Carbon black, at plant		UncertaintyType	standardDeviation95%	GeneralComment			
				GLO 0 kg							
				Location	InfrastructureProcess						
Input from Technosphere	crude oil, at production onshore	RME	kg	1.81E+00	1	1.24	(2,4,2,1,1,5); Based on a assumed yield of 65% (by C-content of 85%)				
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.70E-01	1	1.24	(2,4,2,1,1,5); Data from Ullmann's about two types of carbon black				
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation				
	transport, lorry<16t, fleet average	RER	tkm	9.05E-01	1	2.09	(4,5,na,na,na,na); standard distances				
Output	Carbon black, at plant	GLO	kg	1							
Air emission	Heat, waste		MJ	5.18E+01	1	1.38	(4,3,1,3,3,5); approximation based on Ullmann's				
	Carbon dioxide, fossil		kg	1.97E+00	1	1.38	(4,3,1,3,3,5); calculated from mass balances				
	Carbon monoxide, fossil		kg	8.30E-04	1	6.57	(4,3,1,3,3,5); worst case - based on legal limits				
	Particulates, < 2.5 um		kg	1.00E-03	1	3.94	(4,3,1,3,3,5); based on information in literature				
	Nitrogen oxides		kg	1.05E-03	1	1.97	(4,3,1,3,3,5); based on information in literature				
	Sulfur dioxide		kg	3.30E-03	1	1.38	(4,3,1,3,3,5); based on information in literature				
	PAH, polycyclic aromatic hydrocarbons		kg	1.00E-06	1	1.97	(4,3,1,3,3,5); based on information in literature				

20.6 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

20.7 Conclusions

The inventory for carbon black is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if carbon black is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

20.8 EcoSpold Meta Information

ReferenceFunction	401	Name	Carbon black, at plant
Geography	662	Location	GLO
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	402	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	404	Amount	1
ReferenceFunction	490	LocalName	Russ, ab Werk
ReferenceFunction	491	Synonyms	
ReferenceFunction	492	GeneralComment	The functional unit represent 1 kg of solid carbon black. Large uncertainty of the process data due to weak data on the production process and estimation of data on process emissions.
ReferenceFunction	502	CASNumber	
TimePeriod	601	StartDate	2000
TimePeriod	602	EndDate	2000
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	date of published literature
Geography	663	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	692	Text	Production in a oil-furnace process - using natural gas as further energy input. The overall process yield is of 50%. Inventory bases on literature information about two different types of carbon black. Estimation of emission amount while composition is based on literature.
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	
Representativeness	725	SamplingProcedure	
Representativeness	726	Extrapolations	see technology
Representativeness	727	UncertaintyAdjustments	none

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21 Carbon dioxide

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Review: Heiko Kunst, TU Berlin

Last changes:

2004

21.1 Introduction

Carbon dioxide (CO_2 , CAS-No. 124-38-9) – is a colorless and odourless, non-flammable gas with a slightly sour taste (Topham (1993)). At normal temperature, carbon dioxide is a stable substance – some decomposition is only possible by using high temperature, UV light or electrical discharge. A reaction of CO_2 with other substances needs either high temperature or a catalyst. The most important chemical and physical properties of the liquid form of carbon dioxide are given in Tab. 21.1.

Tab. 21.1 Chemical and physical properties of liquid carbon dioxide (according to BOC Gases (1994))

Property	Unit	Value	Remarks
Molecular weight	44.01	g mol^{-1}	
Melting point	-56.6	°C	At normal pressure
Boiling point	-78.5	°C	At normal pressure
Critical temperature	30	°C	
Vapour Pressure	57.3	Bar	At temperature of 20°C

21.2 Reserves and Resources of material

Carbon dioxide is mainly generated as a by-product e.g. in the production of ammonia or hydrogen. Therefore, all further discussion of resources equals to the discussion about the production of these different substances (see respective chapters within the different reports of ecoinvent).

21.3 Use of material / product

On market, carbon dioxide exists in three different forms – gaseous, liquid and as solid. According to Topham (1993) almost half of the amount of carbon dioxide that is recovered within the different chemical production processes, is used directly in its gaseous form in the close neighbourhood, mainly to produce urea or methanol.

The solid form of carbon dioxide was in the beginning the more important of the remaining two – also called dry ice. It was used mainly as a refrigerant, for food in general and especially for the production of ice-cream. Nowadays, solid carbon dioxide is used only in specific applications – e.g. where weight is a very important factor.

The liquid form is nowadays the dominating non-gaseous form of carbon dioxide. Therefore, it has a variety of different uses:

- *Use as an inert environment:* there are a variety of processes / situations, where air (especially the oxygen part of it) can cause undesirable effects and therefore, carbon dioxide is used instead. This means also, that although liquid carbon dioxide is bought, for the use it has to be first converted into its gaseous form. Examples for this application are e.g. fire extinguishers, shielding gas in arc welding or the handling and transportation of a variety of foodstuff.

- *Promoting the growth of plants:* As carbon dioxide is essential for the plant growth, producers start to introduce additional CO₂ into their greenhouses. This results in higher assimilation rates and an increase of the yield up to 15%.
- *Heat transfer medium:* There are several nuclear power stations that use CO₂ as an intermediate heat transfer medium. It serves in the same time as reactor coolant.
- *Refrigerant:* Especially in the United States, liquid carbon dioxide is used extensively for freezing food as well as for the storage esp. the transport.
- *Chemical uses:* There are a variety of chemical processes that use CO₂ as one of the educts. Examples are e.g. sodium salicylate (intermediate of aspirin production), lead carbonate, sodium carbonate, etc.
- *Others:* Besides, a variety of further uses exist – some of them are described in Topham (1993).

According to Topham (1993), only about half of the CO₂ generated is really recovered, and thereof about 50% are used in close neighbourhood (see above). For the remaining liquid esp. solid part, it is estimated that in the United States several Mio t are produced, in Europe about 1 Mio t and in Japan around 0.5 Mio t. Thereof about 10 to 20% are dry ice – i.e. the solid form of carbon dioxide.

21.4 Systems characterization

As already in chapter 21.2 mentioned, carbon dioxide is extracted from the waste gas of a variety of different industrial production processes. The most important sources are thereby the production of ammonia as well as the production of hydrogen. Another important source is the exploitation of natural gas that is naturally rich in CO₂.

As in all cases carbon dioxide would be released to the air, carbon dioxide is seen as a by-product and not as a co-product of these different production processes. Therefore all environmental burdens from the production process e.g. of ammonia are allocated to ammonia and none of them to carbon dioxide.

Within this study, two forms of CO₂ are further examined – the gaseous and the liquid ones (see chapter 21.5 esp. 21.6). The third form has so low importance that no further investigation concerning dry ice is made within this study here. As process location Europe (RER) is used for both cases.

21.5 Carbon dioxide gaseous, at plant (location: RER)

According to the explication in the antecedent chapters, the gaseous form is mainly used in the direct neighbourhood by another production process. In this study here it is assumed, that gaseous CO₂ is a direct by-product from these other production sites (e.g. ammonia production) and therefore is used free of any environmental burden. Thus, according to the method no dataset “Carbon dioxide gaseous, at plant” has to be established (see Frischknecht et al. (2007)).

21.6 Carbon dioxide liquid, at plant (Location: RER)

21.6.1 Process

For this inventory the functional unit is 1 kg liquid carbon dioxide, as this is nowadays the most commonly bought and sold form of CO₂. The dataset is based on data in Frischknecht (1999) as well as the information from Topham (1993).

The dataset in Frischknecht (1999) represents the extraction as well as the purification of CO₂ from the ammonia production waste gas stream. Its inputs and outputs are summarized in Tab. 21.2. The data are from literature as well as based on personal information from a liquefaction plant.

Tab. 21.2 Input and output values for the production of liquid carbon dioxide (data from Frischknecht (1999))

[per kg CO ₂ liquid]			Remarks
Inputs			
raw materials			
CO ₂ , from ammonia production	kg	2.1	
monoethanolamine	kg	n.a.	no number indicated
energy			
energy, heat	MJ	1.4 - 4.75	MEA-Process: 2 - 4.75 MJ / PC-Process: 1.4 - 2.4 MJ
energy, electricity	MJ	0.72	for purification step
transports			
lorry, 32t	km	150	from recovery to purification
Output			
emissions to air			
carbon dioxide, fossil, to air	kg	1.1	
monoethanolamine, to air	kg	0.008 - 0.018	
impurities, to air	kg	0.01 - 0.03	25% N ₂ +H ₂ , 25% CO ₂ , 50% CH ₄

For this study, the following assumptions and simplifications were used for the dataset “carbon dioxide liquid, at plant”, based on the above shown data:

- *Input of raw material:* In difference to the study from Frischknecht (1999), where the total amount of CO₂ emissions in the ammonia production is allocated to the two different outputs (NH₃, recovered CO₂), in this study here all non-recovered CO₂ – i.e. the reported CO₂ emissions to air – are allocated to the main product of the ammonia synthesis, NH₃. Thus, only the recovered amount is used as starting material for the production of liquefied carbon dioxide.
- *Input of further chemicals:* Nowadays, the most often used processes for the recovery of carbon dioxide are the sodium carbonate, the potassium carbonate as well as the alkanolamine processes. An older process is the use of a 15-20% solution of monoethanolamine (MEA). Due to a lack of information about the new processes, a MEA process is assumed here. Thus, the amount of MEA that is emitted into air has to be added, while the remaining part within the reaction chamber is not taken into account.
- *Energy input:* According to the information in Frischknecht (1999), the average heat consumption for a MEA-process of 3.38 MJ per kg CO₂ is assumed for this study here. A split to gas and fuel according to Frischknecht (1999) is used here. For the electricity consumption in the purification step, the value from Frischknecht (1999) of 0.72 MJ is used. A third, energy consuming step is the liquefaction of the gaseous carbon dioxide. According to Boustead & Hancock (1979), 0.72 MJ are used therefore. For this study, it is assumed that the last one is 100% electricity.
- *Transports:* According to Frischknecht (1999), recovered CO₂ is transported over an average distance of 150 km, before the purification takes place. According to Topham (1993), the cost of transport are very high compared with the production costs. Therefore for this study, it is assumed that the carbon dioxide liquefaction plant is close to the respective source of CO₂ – and thus, no transport of CO₂ is needed. For MEA, standard distances according to Frischknecht et al. (2007) are used.

- *Infrastructure:* For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg ammonium carbonate was included.
- *Emissions to air:* According to Frischknecht (1999), parts of the used chemical (for this study MEA) are emitted to air as well as the different impurities that are taken off during the purification step. For all of them, the same assumption like in Frischknecht (1999) are used here – in case of MEA, the average from the reported range is used.
- *Water input and Emissions to water:* In Frischknecht (1999) there is no information about the use of water within the different process steps. According to Topham (1993) a typical carbon dioxide liquefaction plant using CO₂ from the ammonia production uses as well water for cooling as well as within the process. As there is no quantitative information available in the examined sources, the amount of cooling water used is taken – like for a lot of other chemical substances within this study here – from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In that plant in total an average of 24 kg cooling water per kg of product were used. For the process water it is assumed that 25% of the cooling water amount are used here. According to Topham (1993), the process water is used to remove organic material. Again, no quantitative information is known and therefore, no water emissions are included into this dataset her.
- *Waste:* No information about solid wastes can be found in the examined sources. Therefore waste is neglected in this dataset here.

In the following table the resulting inputs and outputs for the production of 1 kg liquid carbon dioxide, based on all these assumption, are summarized.

Tab. 21.3 Energy demand, material demand and emissions of the production of 1 kg of liquid carbon dioxide (data according to explications in text above).

[per kg liquid carbon dioxide]			Remark
INPUTS			
carbon dioxide containing waste gas	kg	1.015	not included into input data (see text)
monoethanolamine (MEA), at plant	kg	1.30E-02	represents only the lost of chemicals
Water, cooling, unspecified	m ³	2.40E-02	estimation
Water, process, unspecified	m ³	6.00E-03	estimation
Electricity, medium voltage	kWh	0.4	purification & liquefaction energy
heat from heavy fuel oil in industrial furnace	MJ	0.507	split according to Frischknecht 1999
heat from natural gas in industrial furnace	MJ	2.873	split according to Frischknecht 1999
transport by train	tkm	7.80E-03	calculated with standard distances
transport by lorry	tkm	1.30E-03	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.43E+00	calculated from electricity input
carbon dioxide, fossil, to air	kg	5.00E-03	according to Frischknecht 1999
methan, fossil, to air	kg	1.00E-02	according to Frischknecht 1999
monoethanolamine, to air	kg	1.30E-02	according to Frischknecht 1999

21.6.2 Data quality considerations

The following table shows the data quality indicators for the inventory of carbon dioxide production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the carbon dioxide production has quite a high uncertainty, because only few data of the production processes were available. A higher uncertainties exist for the process chemicals demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 21.9.

Tab. 21.4 Input / Output and uncertainty for the process “carbon dioxide liquid, at plant (RER)”

Explanation	Name	Location	Unit	carbon dioxide liquid, at plant		GeneralComment
				RER	uncertaintyType	
				0 kg	StandardDeviations	
					5%	
Resources	Water, cooling, unspecified natural origin	RER	m3	2.40E-02	1	1.9 (5,5,1,1,4,5); estimated with data from a large chem. plant
	Water, unspecified natural origin		m3	6.00E-03	1	1.9 (5,5,1,1,4,5); estimated with data from a large chem. plant
	transport, freight, rail		tkm	7.80E-03	1	2.1 (4,5,na,na,na,na); standard distances
	chemical plant, organics		unit	4.00E-10	1	3.8 (4,5,1,3,5,4); estimation
	monoethanolamine, at plant		kg	1.30E-02	1	2.1 (4,5,1,3,5,4); estimation
	electricity, medium voltage, production UCTE, at grid		kWh	4.00E-01	1	1.3 (2,5,2,1,1,5); purification & liquefaction, based on literature
	heat, natural gas, at industrial furnace >100kW		MJ	2.87E+00	1	1.3 (2,5,2,1,1,5); average form range in Frischknecht 1999
	heat, heavy fuel oil, at industrial furnace 1MW		MJ	5.07E-01	1	1.3 (2,5,2,1,1,5); average form range in Frischknecht 1999
Input from Technosphere	transport, lorry 32t	RER	tkm	1.30E-03	1	2.1 (4,5,na,na,na,na); standard distances
	carbon dioxide liquid, at plant		kg	1		
	Carbon dioxide, fossil		kg	5.00E-03	1	1.3 (2,5,2,1,1,5); according to Frischknecht 1999
	Heat, waste		MJ	1.43E+00	1	1.3 (2,5,2,1,1,5); calculated from electricity input
	Methane, fossil		kg	1.00E-02	1	2.1 (2,5,2,1,1,5); according to Frischknecht 1999
Output air emission	Monoethanolamine	RER	kg	1.30E-02	1	2.1 (2,5,2,1,1,5); average form range in Frischknecht 1999

21.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

21.8 Conclusions

The inventory for carbon dioxide is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if carbon dioxide is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

21.9 EcoSpold Meta Information

ReferenceFunction	Name	carbon dioxide liquid, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	This module contains material and energy input and emissions for the production of liquid carbon dioxide out of waste gases from different production processes. Water consumption and infrastructure have been estimated.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Kohlendioxid flüssig, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represents 1 kg of liquid carbon dioxide. Data are based on a Swiss study about different cooling mediums.
ReferenceFunction	CASNumber	124-38-9
TimePeriod	StartDate	1979
TimePeriod	EndDate	1999
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data based on literature study about different cooling mediums used in Switzerland. Data are assumed to be valuable for European conditions.
Technology	Text	Extraction of carbon dioxide out of waste gas streams from different production processes with a 15-20% MEA (monoethanolamine) solution, followed by a purification and a liquefaction step, using electricity as energy source.
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	Data from literature and own assumptions
Representativeness	Extrapolations	Energy amount and emissions from information in a Swiss study used for European conditions. The CO2 input is a by-product from the antecedent process and has no burdens.
Representativeness	UncertaintyAdjustments	none

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22 Carbon monoxide

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 Review: Heiko Kunst, TU Berlin

22.1 Introduction

This chapter describes the production of carbon monoxide. This chemical is used primarily as a reducing agent in the production of metals, or for the production of hydrogen (shift reaction).

22.2 Reserves and resources of CO

Carbon monoxide is a gaseous compound. It is produced primarily from the incomplete combustion of petroleum, coal and natural gas. CO also occurs naturally, mainly from the oxidation of methane emitted by decaying biomass. (Ullmann's 2002).

22.3 Characterisation of CO

CO, CAS 630-708-0 is a colorless, odorless gas. Its molecular weight is 28 g/mol. CO melts at -205.1 °C and boils at -191.5 °C. CO is highly flammable and toxic. This is because it competes with oxygen for the binding of hemoglobin in the blood.

22.4 Production and use of CO

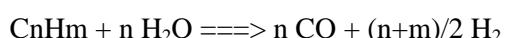
Carbon monoxide is used in a large number of processes. In standard quality, it is used to manufacture phosgene and acetic acid. In extremely pure form, it is used as a component of test and calibration gases, and for manufacturing synthetic diamonds. (www.messergroup.com). Mixtures of hydrogen and CO produced at so-called syngas plants (eg partial oxidation of natural gas) are widely used for the production of methanol. CO is also a common reducing agent for oxides in blast furnaces. (Ullmann's 2002).

22.5 System characterization

Carbon monoxide is produced by basically the same processes that produce hydrogen: steam reforming of light ends (CO₂ reforming), partial oxidation of fossil feedstocks, gasification of coal (Ullmann's 2002). Hydrogen appears as a by-product with all processes that produce CO. To obtain the pure gases, the mixtures must be separated.

22.5.1 CO₂ reforming (Linde, 1988)

Natural gas, refinery gas or light naphtha are fed into a reactor and are heated to 760 - 840 °C and pressurized at 20 – 30 bar in the presence of a catalyst. In addition to the light hydrocarbons, this process requires CO₂. Carbon dioxide reacts with the hydrocarbon feed (CO₂ reforming).. The reformed gas is a mixture of hydrogen, carbon dioxide, carbon monoxide, methane and steam.



Steam reforming (endothermic)

22.5.2 Partial oxidation

Fossil feedstocks, in the density range between natural gas and naphtha.react with oxygen at high temperatures to produce a mixture of hydrogen and carbon monoxide. Due to the high temperature, there

is no catalyst involved, which means that also heavy fuel oil feedstocks can be used. The gas is generated in a pressure vessel at about 1300 – 1400 °C. The resulting gases are cooled by direct-water quench. Soot and solid impurities are washed out.



Source (IPPC Oil & Gas, 2001), (Linde, 1988)

22.5.3 Gasification of coke / coal

Coal is gasified at elevated temperature when reacted with steam and air (oxygen) The water – gas reaction occurs alongside the combustion of coal. Another reaction that occurs is the water – gas shift reaction.



Source (Ullmann's, 2002)

22.5.4 Separation of CO from gas mixtures (Ullmann's 2002)

The CO can be separated from the exit gas mixtures by various means:

- reversible complexation (copper ammonium salt wash) at high pressure, followed by desorption due to pressure drop
- cryogenic separation (e.g. low-temperature partial condensation or liquid methane scrubbing)
- pressure-swing adsorption (PSA) using molecular sieve adsorbents which preferentially adsorb CO or CO₂.

22.6 Life cycle Inventory for carbon monoxide

The following considerations are based on a model plant described in (ChevronTexaco Press Release): A Texaco/Messer plant gasifies approximately 600 metric tonnes per day of low value refinery feedstocks to produce 900 metric tonnes per day of carbon monoxide and up to 25 million standard cubic feet (700'000 cubic meters) per day of hydrogen. The vapor density of hydrogen is 0.082 g/L. This gives 57.4 tons of hydrogen.

22.6.1 Precursors

Tab. 22.1 precursors per kg carbon monoxide (ChevronTexaco Press Release)

Input	Partial oxidation
Heavy fuel oil (5.3% S)	0.66 kg

22.6.2 Energy consumption

Tab. 22.2 energy production / consumption per kg CO

	Partial oxidation
Power consumption	2.3 kWh *

* taken from hydrogen production in (Linde 1992)

It is assumed that any steam required is provided by hydrogen combustion.

22.6.3 Air emissions

Tab. 22.3 air emissions per kg CO

	Partial oxidation
Sulfur dioxide (ppm)	0.0016 *

* taken from hydrogen production in (Linde 1992)

22.6.4 Wastewater emissions

Tab. 22.4 wastewater emissions per kg CO

	Partial oxidation
Wastewater	1.15 kg *

* contains compounds which enter with the oil / coal input, various salts and nickel and vanadium organic compounds. The wastewater is treated and produces sludge. Source: (Linde 1992) figures for hydrogen production

22.6.5 Liquid wastes

The purification of wastewater from the partial oxidation and coal gasification route generates heavy metal-containing sludges (vanadium, nickel). The sludges are treated to remove the metals content. (Linde, 1992)

22.6.6 Solid wastes

Tab. 22.5 solid wastes per kg CO

	Partial oxidation
solid wastes	0.0042 kg slag* *

- glassy sand, figures taken from hydrogen production in (Linde 1992)

22.6.7 Transports and infrastructure

No information was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.000000004 units per kg of produced product.

It is assumed that the heavy fuel oil is directly produced at a refinery, so there are no transport distances considered in this inventory.

22.7 Data quality considerations

Data quality is poor, as it is based on a rough estimate for only one type of carbon monoxide production process.

Tab. 22.6 Input / output data and data quality for carbon monoxide production

Explanations	Name	Location	Unit	carbon monoxide, CO, at plant	Uncertainty Type	Standard Deviation 95%	General Comment
	Location			RER			
	Infrastructure Process			0			
	Unit			kg			
Input from Technosphere	chemical plant, organics	RER	unit	4.00E-10	1	1.32	(4,5,1,1,1,4); infrastructure
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	2.30E+00	1	1.16	(3,3,1,1,1,4); power
	heavy fuel oil, at refinery	RER	kg	6.60E-01	1	1.26	(3,5,1,1,1,4); precursor
Emissions	Heat, waste	-	MJ	8.30E+00	1	1.12	(1,3,1,1,1,4); waste heat
Outputs	carbon monoxide, CO, at plant	RER	kg	1			

22.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

22.9 Conclusions

The inventory for carbon monoxide is based on industry sources, estimations and assumptions. The unit process raw data are meant to be used as background information if CO is used for a product in small amounts. Therefore these data can give a rough approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

22.10 EcoSpold Meta Information

ReferenceFunction	Name	carbon monoxide, CO, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	LocalName	Kohlenmonoxid, CO, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	This report assumes that CO is produced from partial combustion of heavy heating oil. The inventory is based on assumed production figures from a planned plant. Other production pathways were not included, due to a lack of data.
ReferenceFunction	CASNumber	630-08-0
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	RER
Technology	Text	based on literature data and plant data in Europe and North America
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	none
Representativeness	UncertaintyAdjustments	none

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23 Chlorine and Sodium Hydroxide

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Review: Prof. Michael Overcash, USA & Heiko Kunst, TU Berlin

23.1 Introduction

Chlorine (Cl_2 , CAS-No. 7782-50-5) is a greenish-yellow gas with a strong, irritating odor. Chlorine is slightly soluble in water. The most important chemical and physical properties are summarized in Tab. 23.1.

Synonyms for Chlorine: Dichlorine; Molecular Chlorine

Tab. 23.1 Chemical and physical properties of Chlorine (Bentor (2002) / Schmittinger et al. (1993)).

Property	Value	Unit	Property	Value	Unit
Molecular weight	70.906	g mol^{-1}	Melting point	-101	°C
Density (at 0°C)	3.21	kg m^{-3}	Boiling point	-34.6	°C

Sodium hydroxide (NaOH , CAS-No. 1310-73-2) is a white odorless pellet or solid. Sodium hydroxide is very soluble and often used in water solutions. The most important chemical and physical properties are summarized in Tab. 23.2.

Synonyms for NaOH : Caustic soda; Sodium hydrate; Lye; lye, caustic; soda lye; White Caustic;

Tab. 23.2 Chemical and physical properties of Sodium hydroxide (Chemfinder (2002)).

Property	Value	Unit	Property	Value	Unit
Molecular weight	39.997	g mol^{-1}	Melting point	318	°C
Density (at 25°C)	2.13	g cm^{-3}	Boiling point	1390	°C

The following description of reserves, resources and the use of chlorine and sodium hydroxide are summarized from Euro Chlor (1999a), from online information (Euro Chlor (2002a), Euro Chlor (2002b) and Euro Chlor (2002c)) as well as from Schmittinger et al. (1993) and European Commission (2000).

23.2 Reserves and Resources

Most chlorine and sodium hydroxide nowadays is produced from sodium chloride. Therefore, the resources available as well as the reserves are the same as for the production of Sodium chloride, described in Chapter 71.

23.3 Production Technologies and Use

23.3.1 Production technologies for chlorine and sodium hydroxide

Main technology for the production of chlorine and sodium hydroxide is the chlor-alkali process. In this process, chlorine and alkali (sodium hydroxide) are produced by electrolysis of a salt solution. Main technologies therefore are mercury, diaphragm and membrane cell electrolysis. Each of these processes represents thereby a different method to keep the chlorine produced at the anode separate from the caustic soda and hydrogen produced at the cathode, as shown in Fig. 23.1.

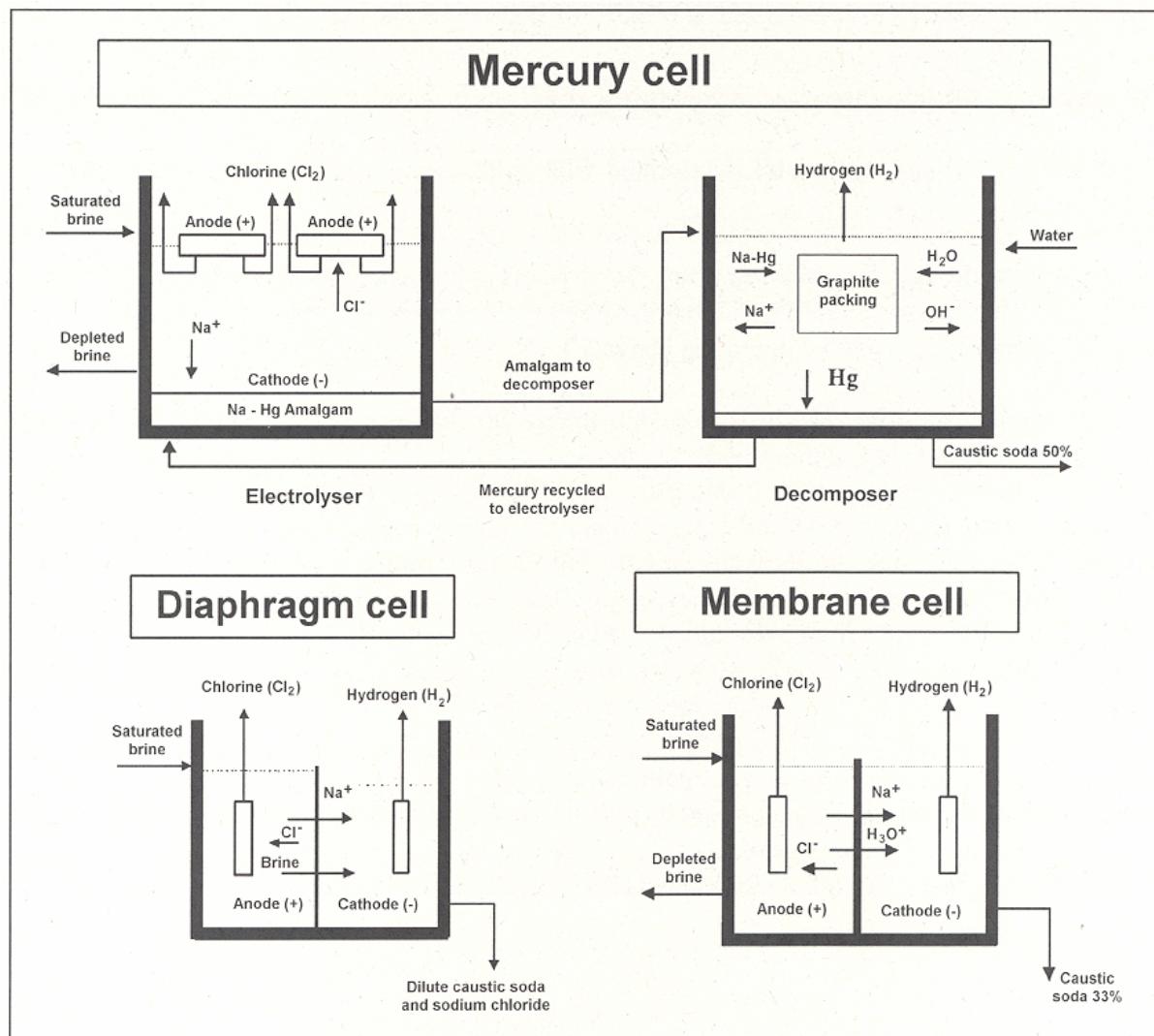


Fig. 23.1 Simplified scheme of chlorine electrolysis cells (Figure 2.2 from European Commission (2000))

In all cases, the following basic principle is used (European Commission (2000): 9):

- **Anode:** chlorine ions are oxidised - chlorine (Cl_2) is formed. The chemical reaction therefore is:

$$2 \text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2 \text{e}^-$$
- **Cathode:** While in the diaphragm and membrane cell, water decomposes to form hydrogen (H_2) and hydroxide ions (OH^-), in the mercury process, a sodium/mercury amalgam (formed at the anode) reacts with water in the decomposer cell (cathode) to form H_2 and OH^- . All in all, the chemical reaction at the cathode is:

$$2 \text{Na}^+(\text{aq}) + 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{Na}^+(\text{aq}) + 2 \text{OH}^-(\text{aq})$$
- To sum up, the **overall reaction** of the electrolysis of the salt solution is the following:

$$2 \text{Na}^+(\text{aq}) + 2 \text{Cl}^-(\text{aq}) + 2 \text{H}_2\text{O} \rightarrow 2 \text{Na}^+(\text{aq}) + 2 \text{OH}^-(\text{aq}) + \text{Cl}_2(\text{g}) + \text{H}_2(\text{g})$$

The mercury cell electrolysis

This technology is in use in Europe - as the first to be performed on an industrial scale - since 1892 and is still dominating the European chlor-alkali industry. A mercury cell system consists of two cells - the electrolyser and the decomposer (see also Fig. 23.1). In the first one, you find anodes of graphite or titanium and a mercury cathode that flows along the bottom of the cell. Due to a direct electrical

current on a salt solution, chlorine is liberated at the anode while sodium dissolves into the mercury cathode to form an amalgam. In the second cell (decomposer), the amalgam reacts with water and produces hydrogen and a 50% sodium hydroxide solution. The so regenerated mercury is returned to the first cell. The whole process is very energy intensive (Euro Chlor (1999a)).

The diaphragm cell electrolysis

Developed also at the end of the 19th century, but mainly in the United States of America, this technique consists of a cell with a usually asbestos diaphragm applied to an iron grid cathode which prevents the chlorine and sodium hydroxide from mixing. Again, hydrogen is produced together with the formation of sodium hydroxide. The whole process needs less energy than a mercury cell, but the sodium hydroxide solution has a concentration of only 10 to 12%. To obtain a sealable NaOH solution, an energy intensive evaporation (water) and precipitation (unreacted salt) process is needed (Euro Chlor (1999a)).

The membrane cell electrolysis

This type of chlor-alkali electrolysis cell was developed around 1970. In this third type, the cell is separated into two compartments by a membrane that acts as an ionexchanger. In the beginning, the anionic compartment is filled with a saturated salt brine, the cathodic one just with water. The main advantages of this third type are the moderate energy consumption (close to the one of the diaphragm cell), the production of more pure sodium hydroxide than a diaphragm cell and the negligible environmental impacts (no Hg and no asbestos emissions !) (Euro Chlor (1999a)).

Auxillary processes before / after electrolysis cell

All three cell types need some common auxillary processes for preparation of the brine as well as the final production and handling of the the products (chlorine, sodium hydroxide and hydrogen). Within the preparation of the salt brine, the following steps can be divided:

- **Brine production:** Usually fresh salt is dissolved in water or in depleted brine from mercury or membrane process. Basic raw material therefore is solid salt.
- **Brine purification:** With this step, undesirable elements that affect the electrolytic process are taken out of the brine. Various chemicals are added to eleminate the different undesirable components. For the membrane cell, a more precise purification is needed - therefore this technology has a second purification step composed of a filter and a softening step using an ion exchange unit.
- **Brine resaturation:** Most plants have installed a brine recirculation and resaturation circuit. In such a recirculation circuit, the brine leaving the electrolysis cell is first dechlorinated (extraction with air - in case of mercury and membrane cells), then the saturation with salt is made. In case that impure salt is used, the pH of the solution is bought to an alkaline level with caustic soda (helps to reduce the solubility of impurities). To protect the anode coating, on the other hand side, hydrochloric acid can be added to bring the pH to an acidic value. This leads probably to the production of carbon dioxide emissions in case where carbonates were introduced into the brine as impurities of the added salt. The process can be in open or in closed vessels.

Concerning the final handling of the different products from the electrolysis process, the following steps have to be mentioned:

- **Chlorine production:** Before chlorine can be used, it goes through several processes for cooling, cleaning, drying, compression and liquefaction. But there exist also several industrial processes that use chlorine as dry gas without need for liquefaction. The cooling step with chilled water serves to reduce the volume of the chlorine gas and to condensate a part of the moisture. In the following

drying step, the water content is further reduced by contact with concentrated sulphuric acid. For the compression step, several different techniques can be used like for the last step, the liquefaction.

- **Sodium hydroxide:** This product is usually sold as a 50% solution. In case of the mercury cell, the process produces directly this solution, while the two other cell types produce a less concentrated solution. Therefore, for the diaphragm and the membrane cell, NaOH has to be concentrated by evaporation with steam as energy source. After some filtration steps to remove impurities (and Hg in case of mercury cell), sodium hydroxide can be stored.
- **Hydrogen:** It leaves the cell already highly concentrated. Therefore it is just cooled to remove moisture and small impurities (NaOH, salt, Hg in mercury cell).

23.3.2 Use

Chlorine and sodium hydroxide have very broad spectrum of use and especially chlorine is a very very important raw material for a variety of different chemical products. VCM² (used in the synthesis of PVC) is in most European countries still main driver for the chlor-alkali production. About 80% of Cl₂-consumption is for organic uses (VCM, chloromethane, phosgene, organic chlorinated solvents, etc.), 16% are for inorganic uses (sodium hypochlorite, HCl, metal chlorides, etc.) and only about 4% are used directly as chlor (mainly for water treatment and in pulp/paper industry). Fig. 23.2 shows the most important areas of application of chlorine in Europe.

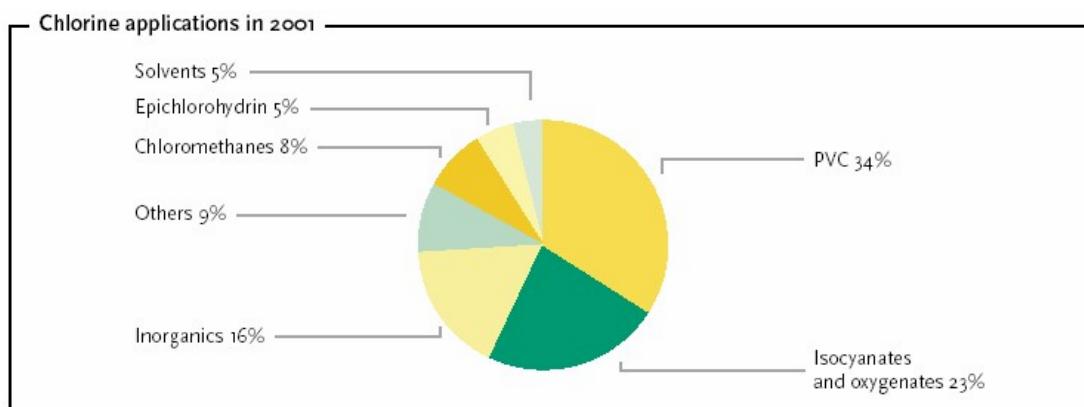


Fig. 23.2 Main applications of chlorine in Europe in 2001 (figure from Euro Chlor (2002b))

Due to the fact that chlorine is very difficult to store and transport it is generally produced near to the consumer. In Europe more than 85% is used on the same site or just nearby for other chemical processes. Sodium hydroxide on the other hand side is very easily stored and transported. The main applications and markets are chemicals (synthesis of other chemicals), metal industry, pulp/paper sector, textile industry, soap & surfactants producer or water treatment - as shown in Fig. 23.3.

² VCM: Vinyl chloride monomer

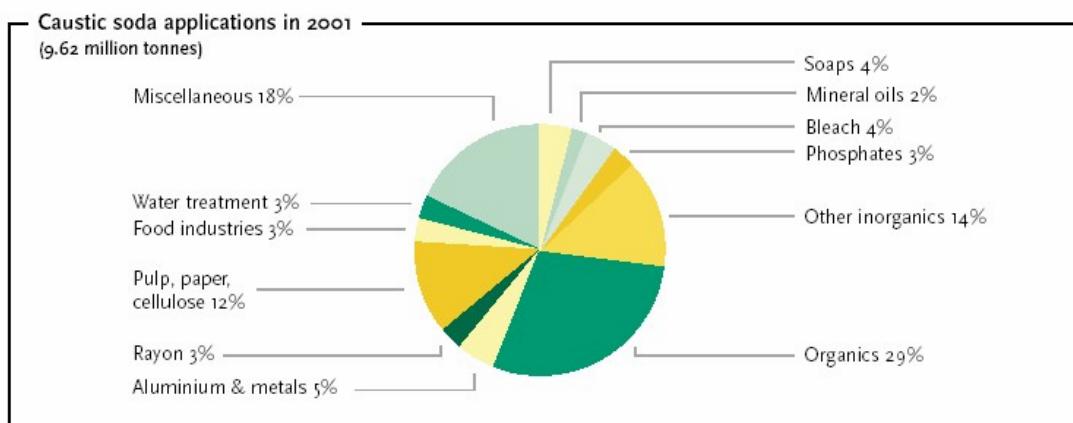


Fig. 23.3 Main applications of sodium hydroxide (caustic soda) in Europe in 2001 (figure from Euro Chlor (2002a))

23.4 System characterization

Western Europe clor-alkali industry is dominated by the mercury cell process. In June 2000, 55% of the capacity consisted of mercury cells, 22% of diaphragm cell and 20% of membrane cells (European Commission (2000)). Therefore, separate modules for these different techniques were established within this project. In each case, the auxillary processes mentioned above (see chapter 23.3.1) are included into the electrolysis cell module - with one exception: the liquefaction step of chlorine is only integrated into the average European chlorine module. Therefore, chlorine is represented in this database as gaseous substance (cell specific modules) and as liquid (average module). Furthermore, average module are also calculated for sodium hydroxide and hydrogen. The whole system is shown here.

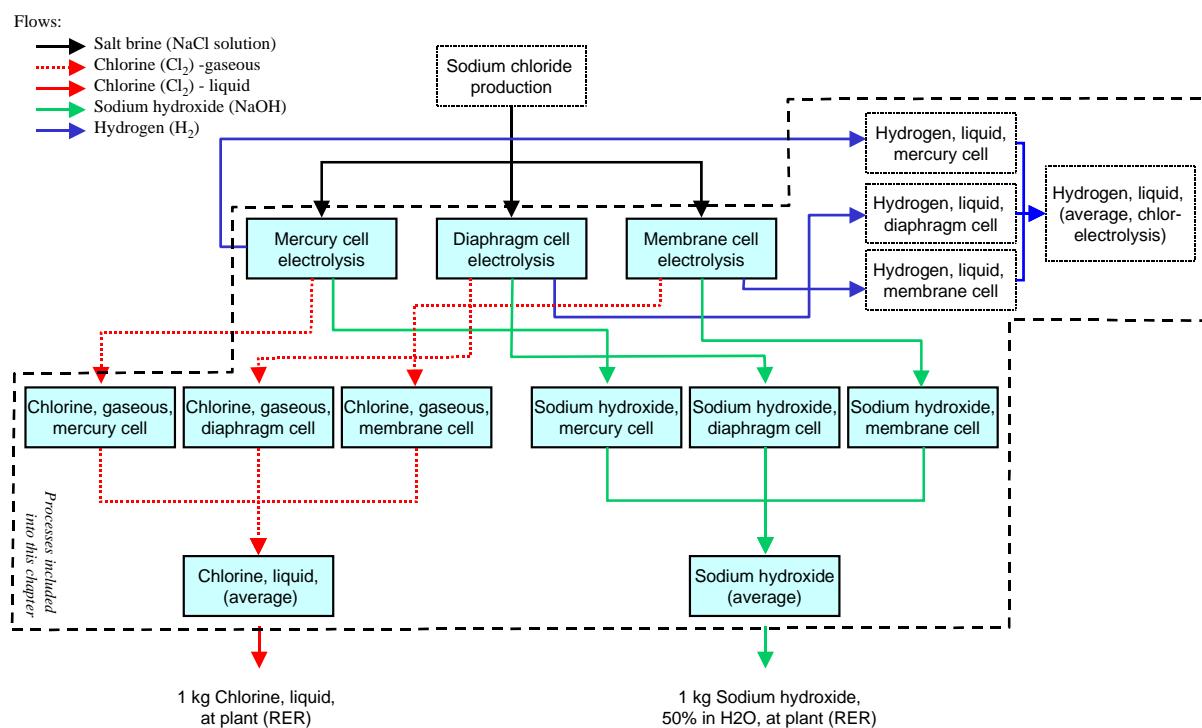


Fig. 23.4 System in database Ecoinvent for production of chlorine (Cl_2) and sodium hydroxide (NaOH)

23.5 Chlor-alkali electrolysis processes

Main data source for the different electrolysis processes is the EC-IPPC³ BAT⁴ documentation about the chlor-alkali industry (European Commission (2000)). This report has as first goal "to reflect accurately the exchange of information as required by the EC IPPC-Directive and to provide reference information for the permitting authority" (European Commission (2000): vii). The document represents therefore a summary of information about present state as well as future improvements possible of the mentioned industry. Additional data sources (Ayres (1997), Landbank (1994)) have been taken into account for plausibility checks and comparison reasons. Explicitly not taken into account are the values from APME (Boustead (1998)) due to the fact that (i) these are only available as cummulated data-sets, thus a comparison is not possible, and (ii) these reflect only the electrolysis processes that are relevant for the European plastics industry and not the total of European electrolysis processes.

23.5.1 Process data

Raw material and Auxillaries

For preparation of the salt brine used within the electrolysis cell, different types of salt are used: vacuum-crystallized salt from solution-mining, rock salt and solar salt. Another possibility is the use of waste brine that comes directly from the exploitation of an underground salt deposit. Due to a lack of information about the market share of the different types of salt, we use in this project the average crystallized salt for Europe like established in chapter 71.

Concerning the amount of salt used, Tab. 23.3 gives an overview of the information about the salt consumption in the different sources used.

Tab. 23.3 Salt consumption for the production of chlorine in the different electrolysis processes

[g/kg chlorine]	Mercury cell	Diaphragm cell	Membrane cell
Stoichiometric consumption		1648	
EU-IPPC BAT report		1750	
Ayres 1997	1711	1712	2430
Landbank 1994	1714	1723	1714
This study	1750	1750	1750

In two cases, the different sources report very similar values while for the membrane cell, one report has a very different value than the other ones. In this case, the value in Ayres (1997) seems too high, leading to an excess concentration of sodium chloride in the resulting brine. Therefore, in this study, the amount reported in European Commission (2000) is used for all three technologies.

Second raw material used - as already seen in the equations of Chapter 23.3.1 - is water. Within the whole process, water is used for preparation of the brine, purges, for maintaining the water balance in the reaction to form sodium hydroxide (in mercury and membrane cells) as well as in the chlorine absorption unit. In the examined literature, the following values for process water consumption can be found.

³ IPPC : Integrated Pollution Prevention and Control

⁴ BAT: Best available technology

Tab. 23.4 Water consumption for the production of chlorine in the different electrolysis processes

[kg water/kg chlorine]	Mercury cell	Diaphragm cell	Membrane cell
Stoichiometric consumption		0.51	
EU-IPPC BAT report		1.0 - 2.8	
Ayres 1997	0.49	0.51	0.50
Landbank 1994	3.32	5.96	3.16
This study	1.9	1.9	1.9

Comparing the information in Ayres (1997) with the stoichiometric consumption (the minimum amount of water needed to fulfil the overall equation shown in Chapter 23.3.1) it can be clearly seen that in this report only the water amount for the reaction is considered. On the other hand side, Landbank (1994) explicitly mentions for each process an amount of 1.66 kg/kg Chlorine for the production of the salt brine. Nevertheless, the total values from this source looks rather high. Therefore, in this study the mean values from the range indicated in European Commission (2000) are used as process water input. The output to the waste water treatment in this study is the difference between process input and stoichiometric consumption.

Additionally, water is used for cooling. There is only one report, indicating values for cooling water consumption with amounts of 100 m³/t Chlorine for mercury and membrane cells and 290 m³ for diaphragm cells (Landbank (1994)). Due to a lack of further information, these values are used within this study.

Besides salt and water, a couple of chemicals are used as auxillary materials in the different steps of the chlor-alkali electrolysis (see chapter 23.3.1). Tab. 23.5 gives an overview about these auxillaries.

Tab. 23.5 Auxillary materials consumption for the production of chlorine in the different electrolysis processes

[per kg chlorine]	EU-IPPC BAT			Ayres 1997			Landbank 1994		
	Hg ¹	Dia ¹	Mem ¹	Hg	Dia	Mem	Hg	Dia	Mem
Mercury	mg	2.6 - 10.9		3					
Asbestos	g		0.1 - 0.3						
Sodium carbonate	g		3 - 20	38.6		34.5	51.5	40.3	49.3
Barium salts	g		3.5						
Calcium chloride	g		0.6 - 35	14.4	12.9				
Hydrochloric acid	g		20 - 30	25.2	56.4	11.4			
Sodium sulphite	g		n.a.	0.112					
Sodium hydroxide	g	3 - 5	0	40			51.5	40.3	49.3
Sodium hydroxide	g		2						
Sulphuric acid	g		15 - 20	8.624	8.7	9.34			
Carbon tetrachloride	g				0.011				

¹ Hg: mercury cell, Dia: diaphragm cell, Mem: membrane cell

Comparing the different sources, there are rather high differences for three substances - sodium carbonate, sodium hydroxide and sulphuric acid. For all other substances, where more than one source indicate a value, these values are of a similar range.

Keeping in mind that European Commission (2000) is representing the most up-to-date information, mainly mean values from its ranges are used within this study. In case of sodium hydroxide, the values from European Commission (2000) are used as they show large technology specific differences and for sulphuric acid the values from Ayres (1997) are used with the same explication. Additionally, sodium sulphite and carbon tetrachloride amounts based on the values in Ayres (1997) are used for all

three technologies due to the fact that the utilization of these two auxillaries is not depending of the electrolysis technology. The resulting input values of auxillaries together with indications about the use of these substances are summarized in Tab. 23.6.

Tab. 23.6 Input values in this study for auxillaries consumption in the production of chlorine

[per kg chlorine]	This study			
	Hg	Dia	Mem	
Mercury mg	6.75	-	-	
Asbestos g	-	0.2	-	
Sodium carbonate g	11.5	11.5	11.5	precipitation Ca-ions
Barium salts g	3.5	3.5	3.5	precipitation of sulphate
Calcium chloride g	17.8	17.8	17.8	precipitation and elimination of sulphate
Hydrochloric acid g	25	25	25	pH adjustements, dechlorination of brine, regeneration ion-exchange resin
Sodium sulphite g	0.1	0.1	0.1	dechlorination of brine
Sodium hydroxide g	4	-	40	removal Mg & heavy metals
	2	2	2	pH control, ion exchange resin
Sulphuric acid g	8.62	8.7	9.34	chlorine drying process
Carbon tetrachloride g	0.01	0.01	0.01	chlorine purifying & liquefying

Energy and Transportation

Concerning the energy demand of the different types of chlorine production cells, Tab. 23.7 gives an overview of the reported energy demand in the different sources available.

Tab. 23.7 Energy consumption for the production of chlorine in the different electrolysis processes

[kWh/kg chlorine]	Electricity			Heat (Steam)			Remarks
	Hg	Dia	Mem	Hg	Dia	Mem	
EU-IPPC BAT report	3.56	2.97	2.79	-	0.61	0.18	Steam out of electricity
Ayres 1997	3.58	2.81	2.80	1486	1.83	0.68	¹
Landbank 1994	3.73	3.05	2.80	187	2.18	0.62	Unknown origin
This study	3.56	2.97	2.79	-	0.61	0.18	

¹ Values in Ayres (1997) are reported in kg. Assumption for transformation to kWh: steam pressure = 4 bar, and therefore a heating value of 2.74 GJ/t steam.

As can be seen from Tab. 23.7, all sources examined have similar values for the electricity consumption in the different cell types. Therefore, in this study the values from the most recent study (European Commission (2000)) are used. In the question of steam consumption, the different sources report very different values. Due to the fact that European Commission (2000) with the most detailed process description is not mentioning other steam consumer than the concentration process of sodium hydroxide up to a 50% solution in case of diaphragm and membrane technology, the values from this source are used within this study. In accordance with European Commission (2000), this steam amount is reported as additional electricity consumption.

Concerning transportation, no information is available in the examined data sources. Therefore, for all auxiliary materials, standard distances and means of transport according to Frischknecht et al. (2007b) were used. For the main input material - salt - it is assumed that the majority of the electrolysis plants are close to their respective salt supplier. In Frischknecht et al. (1996) (Appendix A, p.19), therefore a transport distance of 80 km on the road is assumed. Due to a lack of further information, we continue to use the value of 80 km by lorry for this study. For the transportation of the different wastes pro-

duced within the three electrolysis cell types, again, standard distances and means of transport are used. Tab. 23.8 summarizes the total transport amounts for the production of 1 t of chlorine.

Tab. 23.8 Total transport distances and means for the production of chlorine in the different processes

[tkm/kg chlorine]	Mercury cell		Diaphragm cell		Membrane cell	
	lorry	train	lorry	train	lorry	train
raw material	0.140	-	0.140	-	0.140	-
auxillaries	0.049	0.014	0.044	0.013	0.092	0.021
waste to disposal sites	2.9E-06	-	1.0E-06	-	6.0E-06	-
Total transports	0.189	0.014	0.184	0.013	0.232	0.021

Infrastructure and Land-use

Main part of the infrastructure is the cell room, where all the electrolysis cells of the company are situated. Most of them are placed within a building, with some exceptions, where the cells are not protected. In this study, we examine only the cell systems in a building. From a picture of a 300'000 t/a mercury plant, we estimate a surface of about 3'200 m² just for the electrolysis cells (Euro Chlor (1999b)). Assuming that for all brine preparation and chlorine end processing processes the area is twice of that size (e.g. 6'400 m²) will lead to a total surface of about 10'000 m² or 1 ha. From the capacity it is one of the biggest mercury electrolysis plant in Europe - but no information is available about its technological state and if the land use can be seen as more average or if it is very high/low for a chlorine electrolysis plant.

Therefore, as there are not more information available about any electrolysis plants, in this study, the infrastructure for all types of electrolysis cells is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report.

Emission to air and water

Available information about emissions to air and water is summarized in Tab. 23.9. All information is from the same data source (European Commission (2000)) - the other data sources don't contain much information about emission.

Tab. 23.9 Emissions to air and water of the production of chlorine in the different electrolysis processes

[per kg chlorine]	EU-IPPC BAT			This study		
	Hg	Dia	Mem	Hg	Dia	Mem
<i>Emission to air</i>						
hydrogen	mg	100 - 1000		550	550	550
chlorine	mg	0 - 16		8	8	8
CO2	g	1.2 - 5		3.1	3.1	3.1
mercury	mg	0.2 - 2.1	-	1.15	-	-
asbestos	ug	-	0.04	-	0.04	-
carbon tetrachloride	mg	0.5 - 4		2.25	2.25	2.25
<i>Emission to water</i>						
free oxidants	g	0.001 - 1.5		0.75	0.75	0.75
chlorate	g	0.14 - 4		2.1	2.1	2.1
bromate	mg	0.22 - 550		275	275	275
chloride	g	4 - 25		15	15	15
chlorinated hydrocarbons	mg	0.03 - 1.16		0.6	0.6	0.6
sulphate	g	0.3 - 0.7 (vakuum salt) 15 (rock salt)		7.90	7.90	7.90
mercury	mg	0.01 - 0.65	-	0.33	-	-
asbestos	mg	-	< 30 mg/l	-	20.85 ¹	-

¹ The asbestos emissions to water are calculated, based on the process water output (see above in text) and the assumption that the emissions are 15 mg/L.

In Landbank (1994), the following air emissions are mentioned: mercury cell (13.4g Chlorine, 1.3g Hg and 0.2 g HCl), diaphragm cell (1.1g Chlorine). With one exception, these values are within the ranges mentioned in Tab. 23.9 - the exception is HCl that is not mentioned in this table. Due to a lack of further information about emissions, for most of the reported emissions the mean values of the documented range are taken within this study. In case of sulphate emissions to water, the value is calculated base on the proportion of vakuum and rock salt in the average salt used in this study (see chapter sodium chloride).

Within this study, asbestos emissions are shown as "particulates <2.5" (asbestos to air) rsp. "solids, inorganic" (asbestos to water), while the emissions of free oxidants are not included into the inventory of ecoinvent.

In addition, there is also an emission of waste heat to the air. The amount is - in accordance with Frischknecht et al. (2007b) - similar to the amount of electricity used within the process.

Waste

Considering waste production in the different electrolysis technologies, only two of the examined studies indicate values for waste. The third study (Ayres (1997)) is establishing not a LCA but a material flow analysis (MFA) and therefore indicates the output flows in a different manner - assigned in the mentioned study with "plausible waste breakdown" - indicating the composition of the total waste, but not specifying the type of waste and the further treatment. From the first two studies, Landbank (1994) gives only very general information, divided into "hazardous waste" and "other waste". There is no information about the composition, the origin or the further treatment of these two types of waste.

Therefore, in this study, the wastes indicated in European Commission (2000) rsp. their mean values were used due to the fact that for these ones more information is available. Tab. 23.10 summarizes these informations, used within this study.

Tab. 23.10 Waste in chlorine production

[per kg chlorine]	waste amount			
	Hg	Dia	Mem	
asbestos g	-	0.1	-	
brine filtration sludges g	0.45 (vakuum salt) 30 (rock salt)			Contains calcium carbonate, magnesium hydroxide, ev. barium sulfate - plus in mercury cell: < 150 mg/kg Hg
brine softening sludges g	-	-	0.6	Contains mainly Cellulose, contaminated with iron hydroxide and silica
Mercury-containing sludge and waste sulphuric acid g	0.29	-	-	Mainly activated carbon - Hg-content 10 - 500 g/kg
	8.62	8.7	9.34	Returns to supplier for refortification (Recycling)

Due to a lack of further information, the following assumptions are used within this study for the mentioned types of waste:

- **Asbestos:** Amount 0.1 g/kg chlorine, only in the diaphragm cell. As this waste is of major concern for the human health, as a first approximation the module "disposal, hazardous waste, 0% water, to underground deposit" is used within this study.
- **Brine filtration sludge:** Amount 15.34 g/kg chlorine (from the repartition of rock and vakuum salt used for the alkali process), composition: 47.5% CaCO₃, 47.5% Mg(OH)₂, 5% BaSO₄ (and 0.75 mg/kg Hg in case of mercury cell). Landfilled at a residual material landfill.
- **Brine softening sludge:** Amount 0.6 g/kg chlorine, only in the membrane cell. As this waste consists mainly of cellulose, we use as approximation the module " disposal, paper, 11.2% water, to sanitary landfill".
- **Hg-containing sludge and waste:** It first goes to a distillation step for the removal of mercury. In the remaining waste, an average Hg concentration of 110 mg/kg is assumed. In two examples in European Commission (2000) (table 3.4 and 3.5) it is reported that these wastes are landfilled. In this study, we assume a composition of 110 mg/kg Hg, all the rest carbon and it is deposited in an underground deposit.

Products & Allocation procedures

As you can see from the equations in chapter 23.3.1, the chlorine production causes automatically also the production of sodium hydroxide (NaOH) and of hydrogen (H₂) in more or less fixed proportions. Tab. 23.11 summarizes the amounts of these other products in the different sources examined within this study. It is obvious, that the value for hydrogen production in Landbank (1994) is wrong. For this study, the values from European Commission (2000) are used.

Tab. 23.11 Co-products from the production of chlorine in the different electrolysis processes

[g/kg chlorine]	Mercury cell		Diaphragm cell		Membrane cell	
	NaOH	H ₂	NaOH	H ₂	NaOH	H ₂
Stoichiometric equations	1128.2	28.2	1128.2	28.2	1128.2	28.2
EU-IPPC BAT report	1128	28	1128	28	1128	28
Ayres 1997	1118	27.00	1128	27.24	1143	27.10
Landbank 1994	1120	280	1120	280	1120	280
This study	1128	28	1128	28	1128	28

Due to the fact that three chemical substances are produced, each one with its own market and application area, an allocation of the electrolysis process has to be made. Therefore, a multitude of different approaches exists. In Boustead (1994), several possibilities for the allocation in case of the chlorine production together with the advantages and disadvantages are described.

- An allocation based on **economic properties** is not appropriate due to the fact that the co-production of chlorine and sodium hydroxide in fixed proportions has always been a problem for the chlor industry. The two substances are used in very different applications, having therefore very different markets with each one its own dynamic - thus it is only by chance that the demand for the two substances is coinciding. In fact, depending on which one is dominant, either can be regarded as by-product and the price of both of these varies accordingly much.
- An allocation based on the **energy content** of each substance is not appropriate due to the fact that these different products are not used as fuels.
- An allocation based on the **produced amount** of each chemical has the advantage, that the allocation factors can be clearly determined accordingly to Tab. 23.11. On the other hand side, such a system is not taking into account the very different uses and therefore also the different prices for the three substances.
- Independently of the chosen allocation criteria, there are steps and therefore also inputs that are used only for one of the three products and thus, an allocation on all three products would not be appropriate. In such cases, no allocation is made and the amount is assigned to the respective product that uses this step.

Based on all arguments, an allocation procedure based on the produced mass of the different substances is chosen for this study: 46.4 % chlorine, 52.3 % sodium hydroxide and 1.3 % hydrogen. For parts of the input and output data where a clear assignment to one of the three products is possible, no allocation is done - instead 100% is assigned to the respective product. Tab. 23.12 summarizes these cases.

Tab. 23.12 Data that can be assigned to one of the products and don't need an allocation procedure

Process	Substance(s)	Belongs to		
		Cl2	NaOH	H2
concentrate NaOH to 50% solution	Heat (steam production) input		X	
chlorine drying process	Sulphuric acid input	X		
chlorine purifying	Carbon tetrachloride input	X		
chlorine purifying	Carbon tetrachloride air emissions	X		

23.5.2 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Most of the used data are from the EC-IPPC BAT documentation that summarizes also the present situation. Main concern in this source is that it is not clearly mentioned how many different sample points there are for the different values given, leading to higher uncertainties in the completeness and in the sample size. The input for cooling water has a much higher uncertainty due to the fact, that the value is from an older study that contains no information, how this value was calculated or measured. Two further areas with much higher uncertainties are the transport and infrastructure data. Due to a complete lack of data, assumptions based on Frischknecht et al. (2007b) (transport) resp. the very general module of an organic chemical plant are

used. But, in general the different electrolysis modules have quite a low uncertainty and represent therefore reasonably the European chlorine electrolysis industry.

Tab. 23.13 to Tab. 23.15 summarize the input and output data as well as the uncertainties used for the different electrolysis cell types that produce chlorine, sodium hydroxide and hydrogen. All of these are multi-output models, having the allocation factors mentioned in the last three rows. The values are given for the production of 1 kg of chlorine. Additionally, the most important fields of the ecoinvent meta information from those datasets are listed in chapter 23.9.

Tab. 23.13 Input- / Output-data for the chlorine, sodium hydroxide and hydrogen production with the mercury electrolysis cell (expressed per kg chlorine produced). The last three rows contain the respective allocation factors.

Explanation	Name	Location	Unit	chlor-alkali electrolysis, mercury cell		UncertaintyType	GeneralComment	chlorine, gaseous, mercury cell, at plant	sodium hydroxide, 50% in H ₂ O, mercury cell, at plant	hydrogen, liquid, mercury cell, at plant					
				RER 0 kg											
				Location	InfrastructureProcess										
Input from Technosphere	Water, unspecified natural origin	m3	1.90E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	Water, cooling, unspecified natural origin	m3	1.00E-01	1	1.64 (2.5,3,1.4,5); estimate based on literature source			46.4	52.3	1.3					
	sodium chloride, powder, at plant	RER kg	1.75E+00	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	mercury, liquid, at plant	GLO kg	6.75E-06	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	soda, powder, at plant	RER kg	1.15E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	barite, at plant	RER kg	3.50E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	calcium chloride, CaCl ₂ , at regional storage	CH kg	1.78E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	hydrochloric acid, 30% in H ₂ O, at plant	RER kg	2.50E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	sulphite, at plant	RER kg	1.00E-04	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER kg	6.00E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	sulphuric acid, liquid, at plant	RER kg	8.62E-03	1	1.24 (1.3,3,1.1,5); Data from survey in literature (Ayres 1997)			100	0	0					
	carbon tetrachloride, at plant	RER kg	1.00E-05	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			100	0	0					
	electricity, medium voltage, production UCTE, at grid	UCTE kWh	3.56E+00	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	transport, lorry 32t	RER tkm	1.89E-01	1	2.09 (4.5,n.a.,n.a.,n.a.,n.a.); Standard distances			46.4	52.3	1.3					
Waste	transport, freight, rail	RER tkm	1.40E-02	1	2.09 (4.5,n.a.,n.a.,n.a.,n.a.); Standard distances			46.4	52.3	1.3					
	chemical plant, organics	RER unit	4.00E-10	1	3.77 (4.5,1.35,4); Estimation			46.4	52.3	1.3					
	disposal, sludge, NaCl electrolysis Hg 0% water, to residual material landfill	CH kg	1.53E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
Output	disposal, spent activated carbon with mercury, 0% water, to underground deposit	DE kg	2.90E-04	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	chlorine, gaseous, mercury cell, at plant	RER kg						100	0	0					
	sodium hydroxide, 50% in H ₂ O, mercury cell, at plant	RER kg	1.128					0	100	0					
Air emissions	hydrogen, liquid, mercury cell, at plant	RER kg	0.028					0	0	100					
	Heat, waste	MJ	1.28E+01	1	1.22 (1.3,1.1,1.5); Calculated (based on Electricity input)			46.4	52.3	1.3					
	Hydrogen	kg	5.50E-04	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	Chlorine	kg	8.00E-06	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	Carbon dioxide, fossil	kg	3.10E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	Mercury	kg	1.15E-06	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	Methane, tetrachloro-, CFC-10	kg	2.25E-06	1	2.05 (1.3,1.1,1.5); EC IPPC study 2002			100	0	0					
	Chlorate	kg	2.10E-03	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	Bromate	kg	2.75E-04	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	Chloride	kg	1.50E-02	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
Water emissions	Chlorinated solvents, unspecified	kg	6.00E-07	1	3.05 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	Sulfate	kg	7.90E-03	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					
	Mercury	kg	3.30E-07	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002			46.4	52.3	1.3					

Tab. 23.14 Input- / Output-data for the chlorine, sodium hydroxide and hydrogen production with the diaphragm electrolysis cell (expressed per kg chlorine produced). The last three rows contain the respective allocation factors.

Explanation	Name	Location	Unit	chlor-alkali electrolysis, diaphragm cell			GeneralComment	chlorine, gaseous, diaphragm cell, at plant	sodium hydroxide, 50% in H ₂ O, diaphragm cell, at plant	hydrogen, liquid, diaphragm cell, at plant
				RER	0	standardDeviation5%				
				kg	kg	standardDeviation5%				
Ressource	Water, unspecified natural origin	m3	1.90E-03	1	1.22	(1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
input from Technosphere	Water, cooling, unspecified natural origin	m3	2.90E-01	1	1.64	(2.5,3.1,4.5); estimate based on literature source	46.4	52.3	1.3	
	sodium chloride, powder, at plant	RER	kg	1.75E+00	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	asbestos, cryostile type, at plant	GLO	kg	2.00E-04	1	1.22 (...); EC IPPC study 2002	46.4	52.3	1.3	
	soda, powder, at plant	RER	kg	1.15E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	barite, at plant	RER	kg	3.50E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	calcium chloride, CaCl ₂ , at regional storage	CH	kg	1.78E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	hydrochloric acid, 30% in H ₂ O, at plant	RER	kg	2.50E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	sulphite, at plant	RER	kg	1.00E-04	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	2.00E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	sulphuric acid, liquid, at plant	RER	kg	8.70E-03	1	1.24 (1.3,3.1,1.5); Data from survey in literature (Ayres 1997)	100	0	0	
	carbon tetrachloride, at plant	RER	kg	1.00E-05	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	100	0	0	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.58E+00	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	38.74	60.18	1.08	
	transport, lorry 32t	RER	tkm	1.84E-01	1	2.09 (4.5,n.a.,n.a.,n.a.); Standard distances	46.4	52.3	1.3	
	transport, freight, rail	RER	tkm	1.30E-02	1	2.09 (4.5,n.a.,n.a.,n.a.); Standard distances	46.4	52.3	1.3	
Waste	chemical plant, organics	RER	unit	4.00E-10	1	3.77 (4.5,1.3,5.4); Estimation	46.4	52.3	1.3	
	disposal, sludge, NaCl electrolysis, 0% water, to residual material landfill	CH	kg	1.53E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	disposal, hazardous waste, 0% water, to underground deposit	DE	kg	1.00E-04	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
Output	chlorine, gaseous, diaphragm cell, at plant	RER	kg	1			100	0	0	
	sodium hydroxide, 50% in H ₂ O, diaphragm cell, at plant	RER	kg	1.13			0	100	0	
	hydrogen, liquid, diaphragm cell, at plant	RER	kg	0.028			0	0	100	
Air emissions	Heat, waste	MJ	1.29E+01	1	1.22 (1.3,1.1,1.5); Calculated (based on Electricity input)	38.74	60.18	1.08		
	Hydrogen	kg	5.50E-04	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Chlorine	kg	8.00E-06	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Carbon dioxide, fossil	kg	3.10E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Particulates, < 2.5 um	kg	4.00E-11	1	2.05 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
Water emissions	Methane, tetrachloro-, CFC-10	kg	2.25E-06	1	2.05 (1.3,1.1,1.5); EC IPPC study 2002	100	0	0		
	Chlorate	kg	2.10E-03	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Bromate	kg	2.75E-04	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Chloride	kg	1.50E-02	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Chlorinated solvents, unspecified	kg	6.00E-07	1	3.05 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Sulfate	kg	7.90E-03	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Solids, inorganic	kg	2.09E-05	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		

Tab. 23.15 Input- / Output-data for the chlorine, sodium hydroxide and hydrogen production with the membrane electrolysis cell (expressed per kg chlorine produced). The last three rows contain the respective allocation factors.

Explanation	Name	Location	Unit	chlor-alkali electrolysis, membrane cell			GeneralComment	chlorine, gaseous, membrane cell, at plant	sodium hydroxide, 50% in H ₂ O, membrane cell, at plant	hydrogen, liquid, membrane cell, at plant
				RER	0	standardDeviation5%				
				kg	kg	standardDeviation5%				
Ressource	Water, unspecified natural origin	m3	1.90E-03	1	1.22	(1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
input from Technosphere	Water, cooling, unspecified natural origin	m3	1.00E-01	1	1.64	(2.5,3.1,4.5); estimate based on literature source	46.4	52.3	1.3	
	sodium chloride, powder, at plant	RER	kg	1.75E+00	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	soda, powder, at plant	RER	kg	1.15E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	barite, at plant	RER	kg	3.50E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	calcium chloride, CaCl ₂ , at regional storage	CH	kg	1.78E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	hydrochloric acid, 30% in H ₂ O, at plant	RER	kg	2.50E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	sulphite, at plant	RER	kg	1.00E-04	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	4.20E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	sulphuric acid, liquid, at plant	RER	kg	9.34E-03	1	1.22 (1.3,3.1,1.5); Data from survey in literature (Ayres 1997)	100	0	0	
	carbon tetrachloride, at plant	RER	kg	1.00E-05	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	100	0	0	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	2.97E+00	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	43.59	55.19	1.22	
	transport, lorry 32t	RER	tkm	2.32E-01	1	2.09 (4.5,n.a.,n.a.,n.a.); Standard distances	46.4	52.3	1.3	
	transport, freight, rail	RER	tkm	2.10E-02	1	2.09 (4.5,n.a.,n.a.,n.a.); Standard distances	46.4	52.3	1.3	
Waste	chemical plant, organics	RER	unit	4.00E-10	1	3.77 (4.5,1.3,5.4); Estimation	46.4	52.3	1.3	
	disposal, sludge, NaCl electrolysis, 0% water, to residual material landfill	CH	kg	1.53E-02	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
	disposal, paper, 11.2% water, to sanitary landfill	CH	kg	6.00E-04	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3	
Output	chlorine, gaseous, membrane cell, at plant	RER	kg	1			100	0	0	
	sodium hydroxide, 50% in H ₂ O, membrane cell, at plant	RER	kg	1.13			0	100	0	
	hydrogen, liquid, membrane cell, at plant	RER	kg	0.028			0	0	100	
Air emissions	Heat, waste	MJ	1.07E+01	1	1.22 (1.3,1.1,1.5); Calculated (based on Electricity input)	43.59	55.19	1.22		
	Hydrogen	kg	5.50E-04	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Chlorine	kg	8.00E-06	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Carbon dioxide, fossil	kg	3.10E-03	1	1.22 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Methane, tetrachloro-, CFC-10	kg	2.25E-06	1	2.05 (1.3,1.1,1.5); EC IPPC study 2002	100	0	0		
Water emissions	Chlorate	kg	2.10E-03	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Bromate	kg	2.75E-04	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Chloride	kg	1.50E-02	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Chlorinated solvents, unspecified	kg	6.00E-07	1	3.05 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		
	Sulfate	kg	7.90E-03	1	1.56 (1.3,1.1,1.5); EC IPPC study 2002	46.4	52.3	1.3		

23.6 Average European chlorine and sodium hydroxide

As already shown in Chapter 23.4, the European chlor-alkali industry is dominated by the mercury cell electrolysis (55% of capacity), followed by diaphragm cells (22%) and membrane cells (20%). The total chlorine production in 2000 in Western Europe totalled 9.7 Mio tonnes (Euro Chlor (2001)) which equals a capacity utilisation rate of 89.6%. In Euro Chlor (2002c) the following rates are shown for the different production routes of chlorine: 54% mercury, 23% diaphragm and 21% membrane cell and 2% from other systems. Therefore, for this study that includes only the three first systems, the following distribution is used to calculate the average European production of chlorine and sodium hydroxide: 55.1% mercury, 23.5% diaphragm and 21.4% membrane cell.

As mentioned in the characterisation of the whole system, the liquefaction step is included into the average module. The only input for this step is energy consumption. Therefore, an electricity consumption of 70 kWh/t gaseous chlorine is used according to the information from a European chlorine producer.⁵ Accordingly to the methodology in this study (see Frischknecht et al. (2007b)), a similar outflow as "waste heat" has to be added. If the reader needs the liquefaction step for one specific cell type, he has here all information needed to establish himself the respective module.

Tab. 23.16 and Tab. 23.17 summarize the resulting input data as well as the uncertainty values for the average chlorine and sodium hydroxide modules of the database Ecoinvent. The uncertainty is very small due to the fact, that data from EuroChlor, representing the European electrolysis plants, for the year 2000 have been used. Additionally, the most important fields of the ecospold meta information from those datasets are listed in chapter 23.9.

Tab. 23.16 Input data for average chlorine production in Europe

Explanation	Name	Location	Unit	chlorine, liquid, production mix, at plant	RER o kg	uncertaintyType	standardDeviation95%	GeneralComment	
								Location	InfrastructureProcess
								Unit	
Input from Technosphere	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	7.00E-02	1	1.22	(1,3,1,3,1,5); data from 1 European chlorine producer		
	chlorine, gaseous, mercury cell, at plant								
	chlorine, gaseous, diaphragm cell, at plant								
	chlorine, gaseous, membrane cell, at plant								
Output Air emissions	chlorine, liquid, production mix, at plant	RER	kg	1					
	Heat, waste		MJ	2.52E-01	1	1.22	(1,3,1,3,1,5); Calculated (based on Electricity input)		

Tab. 23.17 Input data for average sodium hydroxide production in Europe

Explanation	Name	Location	Unit	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER o kg	uncertaintyType	standardDeviation95%	GeneralComment	
								Location	InfrastructureProcess
								Unit	
Input from Technosphere	sodium hydroxide, 50% in H ₂ O, mercury cell, at plant	RER	kg	5.51E-01	1	1.05	(1,1,1,1,1,1); statistics from EuroChlor		
	sodium hydroxide, 50% in H ₂ O, diaphragm cell, at plant								
	sodium hydroxide, 50% in H ₂ O, membrane cell, at plant								
	sodium hydroxide, 50% in H ₂ O, production mix, at plant								
Output	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	1					

As several times shown above, besides NaOH and Cl₂ also H₂ is produced during the chlor-alkali electrolysis. The hydrogen production in general is described in Chapter 41. As mentioned there, H₂ from

⁵ personal communication from a European chlorine producer, September 23, 2002.

the chlor-alkali industry is only a small part of the total production. The average value is calculated here similar to the average value of chlorine and sodium hydroxide. The resulting input data are shown in Tab. 23.18. In Chapter 41 these are used for the calculation of the European average hydrogen production. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 23.9.

Tab. 23.18 Input data for average hydrogen production from electrolysis cells in Europe

Explanation	Name	Location	Unit	<i>hydrogen, liquid, from chlorine electrolysis, production mix, at plant</i>		uncertaintyType	standardDeviation5%	GeneralComment			
				<i>RER 0 kg</i>							
		Location	InfrastructureProcess								
		Unit									
Input from Technosphere	hydrogen, liquid, mercury cell, at plant	RER	kg	5.51E-01	1	1.05	(1,1,1,1,1,1); statistics from EuroChlor				
	hydrogen, liquid, diaphragm cell, at plant	RER	kg	2.35E-01	1	1.05	(1,1,1,1,1,1); statistics from EuroChlor				
	hydrogen, liquid, membrane cell, at plant	RER	kg	2.14E-01	1	1.05	(1,1,1,1,1,1); statistics from EuroChlor				
Output	hydrogen, liquid, from chlorine electrolysis, production mix, at plant	RER	kg	1							

23.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

23.8 Conclusions

Average European datasets for the production of chlorine, sodium hydroxide and hydrogen out of the electrolysis process for the year 2000 are established. Furthermore, datasets representing a weighted mix of the different technologies are established as well.

All these datasets are in accordance with the present quality guidelines of the ecoinvent project and are based on a report covering the European industry, based on statistics for the year 2000. The data are thus of a good quality and can be used in a very broad context.

23.9 EcoSpold Meta Information

ReferenceFunction	Name	chlor-alkali electrolysis, mercury cell	chlor-alkali electrolysis, diaphragm cell	chlor-alkali electrolysis, membrane cell
Geography	Location	RER	RER	RER
ReferenceFunction	InfrastructureProcess	0	0	0
ReferenceFunction	Unit	kg	kg	kg
ReferenceFunction	IncludedProcesses	Besides the electrolysis process in a mercury cell, the following process steps are included into this process: brine production, brine purification, brine resaturation as well as the final handling of the electrolysis products, without the chlorine liquification!	Besides the electrolysis process in a diaphragm cell, the following process steps are included into this process: brine production, brine purification, brine resaturation as well as the final handling of the electrolysis products, without the chlorine liquification!	Besides the electrolysis process in a membrane cell, the following process steps are included into this process: brine production, brine purification, brine resaturation as well as the final handling of the electrolysis products, without - the chlorine liquification!
ReferenceFunction	Amount	1	1	1
ReferenceFunction	LocalName	Chlor-Alkali Elektrolyse, Amalgam-Verfahren	Chlor-Alkali Elektrolyse, Diaphragma-Verfahren	Chlor-Alkali Elektrolyse, Membran-Verfahren
ReferenceFunction	Synonyms			
ReferenceFunction	GeneralComment	The multioutput-process "chlor-alkali electrolysis, mercury cell" delivers the co-products "chlorine, gaseous, mercury cell, at plant", "sodium hydroxide, 50% in water, mercury cell, at plant" and "hydrogen, liquid, mercury cell, at plant". The allocation is done according to the masses of the different products - i.e. 46.4% chlorine - 52.3% sodium hydroxide and 1.3% hydrogen.	The multioutput-process "chlor-alkali electrolysis, diaphragm cell" delivers the co-products "chlorine, gaseous, diaphragm cell, at plant", "sodium hydroxide, 50% in water, diaphragm cell, at plant" and "hydrogen, liquid, diaphragm cell, at plant". The allocation is done according to the masses of the different products - i.e. 46.4% chlorine - 52.3% sodium hydroxide and 1.3% hydrogen.	The multioutput-process "chlor-alkali electrolysis, membrane cell" delivers the co-products "chlorine, gaseous, membrane cell, at plant", "sodium hydroxide, 50% in water, membrane cell, at plant" and "hydrogen, liquid, membrane cell, at plant". The allocation is done according to the masses of the different products - i.e. 46.4% chlorine - 52.3% sodium hydroxide and 1.3% hydrogen.
ReferenceFunction	CASNumber			
TimePeriod	StartDate	2000-01	2000-01	2000-01
TimePeriod	EndDate	2000-12	2000-12	2000-12
TimePeriod	DataValidForEntirePeriod	1	1	1
TimePeriod	OtherPeriodText			
Geography	Text	European average values	European average values	European average values
Technology	Text	present state of technology used in european mercury cells	present state of technology used in european diaphragm cells	present state of technology used in european membrane cells
Representativeness	Percent			
Representativeness	ProductionVolume	unknown	unknown	unknown
Representativeness	SamplingProcedure	Average values from the ranges indicated in EC IPPC-BAT document are used	Average values from the ranges indicated in EC IPPC-BAT document are used	Average values from the ranges indicated in EC IPPC-BAT document are used
Representativeness	Extrapolations			
Representativeness	UncertaintyAdjustments			

ReferenceFunction	Name	chlorine, liquid, production mix, at plant	sodium hydroxide, 50% in H ₂ O, production mix, at plant	hydrogen, liquid, from chlorine electrolysis, production mix, at plant
Geography	Location	RER	RER	RER
ReferenceFunction	InfrastructureProcess	0	0	0
ReferenceFunction	Unit	kg	kg	kg
ReferenceFunction	IncludedProcesses	Process establishing an average European chlorine production from the three different electrolysis cell technologies (mercury, diaphragm, membrane). This process includes additionally the energy consumption for the liquefaction step from gaseous to liquid chlorine.	Process establishing an average European sodium hydroxide production from the three different electrolysis cell technologies (mercury, diaphragm, membrane)	Process establishing an average European hydrogen production from the three different electrolysis cell technologies (mercury, diaphragm, membrane)
ReferenceFunction	Amount	1	1	1
ReferenceFunction	LocalName	Chlor, flüssig, ab Werk	Natriumhydroxid, 50% in H ₂ O, ab Werk	Wasserstoff, flüssig, von Elektrolysezellen, ab Werk
ReferenceFunction	Synonyms	Dichlorine	Caustic soda//Sodium hydrate//Lye//lye, caustic//soda lye//White Caustic//	
ReferenceFunction	GeneralComment	Modul that establishes only an average of the different technologies used for chlorine production - thus no process-specific emissions are included into this dataset.	Modul that establishes only an average of the different technologies used for sodium hydroxide production - thus no process-specific emissions are included into this dataset.	Modul that establishes only an average of the different technologies used for hydrogen production (as co-product of chlorine) - thus no process-specific emissions are included into this dataset.
ReferenceFunction	CASNumber	7782-50-5	1310-73-2	1333-74-0
TimePeriod	StartDate	2000-01	2000-01	2000-01
TimePeriod	EndDate	2000-12	2000-12	2000-12
TimePeriod	DataValidForEntirePeriod	1	1	1
TimePeriod	OtherPeriodText			
Geography	Text	European average values	European average values	European average values
Technology	Text	see general comments	see general comments	see general comments
Representativeness	Percent	100	100	100
Representativeness	ProductionVolume	European Cl ₂ production in 2000: 9697265 tonnes	Equivalent of NaOH from European Cl ₂ production in 2000 of 9697265 tonnes	Equivalent of H ₂ from European Cl ₂ production in 2000 of 9697265 tonnes
Representativeness	SamplingProcedure	Official statistics from the Association of European Chlorine Producers (EuroChlor)	Official statistics from the Association of European Chlorine Producers (EuroChlor)	Official statistics from the Association of European Chlorine Producers (EuroChlor)
Representativeness	Extrapolations			
Representativeness	UncertaintyAdjustments			

23.10 References

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24 Chloromethanes and Tetrachloroethylene

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Last change:

2004

24.1 Introduction

Methyl chloride

Methyl chloride (CH_3Cl , CAS-No. 74-87-3) or monochloromethane is a colourless, almost odourless gas. It is highly explosive and flammable. The toxic gas is a known carcinogen. Liquid methyl chloride will cause burns in contact with the skin (Wells (1991)).

Dichloromethane

Dichloromethane (CH_2Cl_2 , CAS-No. 75-09-2) or methylene dichloride is a clear, colourless liquid with a distinctive, ether-like odour. It is non-flammable under normal storage conditions. Liquid dichloromethane is irritating to skin and eyes (Wells (1991)).

Trichlorethylene

Trichlorethylene (C_2HCl_3 , CAS-No. 79-01-6) known also as TRI, TCE, ethylene trichloride or trichloroethene is a colourless liquid with a sweet odour similar to chloroform. It is non-flammable under normal storage conditions, having no measurable flash point. The flammable limits in air are within 12.3 – 55.3 vol.% (Wells (1991)).

Tetrachloroethylene

Tetrachloroethylene (C_2Cl_4 , CAS-No. 127-18-4) known also as PER or perchloroethylene is a clear, colourless liquid with a distinctive, somewhat ether-like odour. It is non-flammable, having no measurable flash point or flammable limits in air.

For this inventory the functional unit is 1 kg of methyl chloride, dichloromethane, trichloroethylene, and tetrachloroethylene respectively. The most important chemical and physical properties of the substances used in this inventory are given in Tab. 24.1.

Tab. 24.1 Physical properties of methyl chloride dichloromethane, trichloroethylene, and tetrachloroethylene (Wells (1991))

Property	Unit	Methyl chloride	Dichloromethane	Trichloroethylene	Tetrachloroethylene	Remarks
Molecular weight	g mol ⁻¹	50.49	84.94	131.4	165.8	
Specific gravity	kg m ⁻³	0.916 (liquid)	1.326	1.46	1.623	at 20 °C
Boiling point	°C	-27.3	39.75	87.2	121	

24.2 Reserves and Resources of material

Methyl chloride

Commercial production of methyl chloride is based on two different methods. The hydrochlorination of methanol using hydrogen chloride and by chlorinating methane. Methanol hydrochlorination has become increasingly important because this process consumes hydrogen chloride rather than producing it. Also the availability of low-cost methanol, its facile transport and storage is advantageous compared to the methane route (Häussinger et al. (2000)). For this inventory, data of Boustead (1997b) were used, which include both production routes. These data represent 78% of the annual European production of chloromethanes.

Dichloromethane

Commercial production of dichloromethane is based on chlorinating methane-methyl chloride in the gaseous phase. In this process also methyl chloride, chloroform and carbon tetrachloride are obtained. For this inventory data of Boustead (1997b) were used. These data represent 78% of the annual European production of chloromethanes.

Trichloroethylene

For the production of trichloroethylene either acetylene or ethylene is used as a feedstock. The acetylene route, which is still used in Europe comprises acetylene chlorination to trichloroethylene. In the ethylene-based processes, which are widely used in the U.S. and Japan, tetrachloroethylene is obtained as a byproduct in substantial amounts. For this inventory data of Boustead (1997a) were used, which include data from 104'000 t a⁻¹ trichloroethylene production. This inventory covers 90% of the total European production of trichloroethylene.

Tetrachloroethylene

Tetrachloroethylene is mostly co-produced together with trichloroethylene by the chlorinated oxychlorination of ethylene dichloride. A further process to produce tetrachloroethylene is the chlorinolysis of chlorinated wastes. For this inventory data of Boustead (1997a) were used, which include data from 164'000 t a⁻¹ tetrachloroethylene production. This inventory covers 76% of the total European production of tetrachloroethylene.

24.3 Use of material / product

Methyl chloride

Manufacture of methyl chloride (monochloromethane) is the second most common process in the chlorinated aliphatic industry. Some facilities manufacture methyl chloride as an intermediate, which is consumed in the production of silicones. Other facilities manufacture methyl chloride as the first step in an integrated chlorinated methane process. More than 50% of the methyl chloride produced in Europe is used within the production of silicones (Häussinger et al. (2000)).

For this inventory it was assumed that the methyl chloride used in Switzerland is produced in Europe. It was assumed that the main supply for Switzerland origin from Germany. Large producers (>30'000 t a⁻¹) of methyl chloride in Europe are Bayer, Hoechst and Wacker Chemie in Germany, Atochem in France and ICI in the United Kingdom (Wells (1991)).

Dichloromethane

Most of the dichloromethane (methylene dichloride) produced is used as a solvent degreaser and paint remover. It is also used as an extractant solvent for plastic production. Some facilities manufacture methyl chloride as an intermediate, which is consumed in the production of silicones. Other facilities manufacture methyl chloride as the first step in an integrated chlorinated methane process.

Large producers ($>30'000 \text{ t a}^{-1}$) of dichloromethane in Europe are Hoechst and Dow in Germany, Atochem and Solvay in France and ICI in the United Kingdom (Wells (1991)).

Trichloroethylene

The production of trichloroethylene for 1984 is estimated approximately 110'000 t for the U.S., 80'000 t for Japan, and ca. 200'000 t for Western Europe. Since then, however, the production rate of trichloroethylene has declined not only because of reduced losses by improved degreasing systems, but also because of strong competition and replacement by 1,1,1-trichloroethane.

The major outlet of trichloroethylene is in the dry cleaning of fabrics where it is popular because of its low toxicity and non-flammability. Other uses are metal degreasing, electroplate cleaning, extraction of oils and fats, paint removal, dissolving rubber, and sulphur recovery. Additionally trichloroethylene can be used as a chemical intermediate in the manufacture of chlorinated fluorocarbons.

Large production plants ($>35'000 \text{ t a}^{-1}$) in Europe are Atochem and Solvay in France, Enichem and Montedipe in Italy, and ICI in the United Kingdom (Wells (1991)).

Tetrachloroethylene

In 1994, six companies in the EU produced 164'000 t tetrachloroethylene. Sales totalled 78'000 tonnes and exports, 20'000 t. The remainder was used by the chemical industry as an intermediate. EU production and use of the product fell from 340'800 t in 1986 to 164,000 t in 1994.

The main uses of tetrachloroethylene are dry cleaning where it is the main substitute for the solvents, 1,1,1-trichloroethane and R113. Some 60'000 t were used in 1991 by about 60'000 dry-cleaning shops. Further uses include metal cleaning and degreasing, chemical synthesis for production of the CFC substitutes, but the use for chemical synthesis continues to decline.

Large producers ($>35'000 \text{ t a}^{-1}$) of tetrachloroethylene in Europe are Hüls, Wacker Chemie and Dow in Germany, Atochem in France, Enichem and Montefluos in Italy and ICI in the United Kingdom (Wells (1991)).

24.4 Systems characterization

The processes for methyl chloride, dichloromethane, trichloroethylene, and tetrachloroethylene were assessed with data from Boustead (1997b) and Boustead (1997a). Due to the fact that those datasets are cumulated it was not possible to use the other processes modelled in Ecoinvent to obtain a transparent process chain. The data were nevertheless used because it represents a high share of the European production of those chemicals. The transformation for the data as given in Boustead (1997b) and Boustead (1997a) to the data format in Ecoinvent is described in detail in the methodology part of Hischier (2007). Within the modules assessed here there are only the resources and emissions considered which are given in the data source. Therefore, no land use could be included and no direct soil emissions within the process chain are stated. For each waste type described in the methodology used in the datasets of Boustead (1999) an appropriate waste process from the Ecoinvent modules was included.

The following processes were modelled:

- Methyl chloride, at plant (Location: WEU), see Fig. 24.1
- Dichloromethane, at plant (Location: RER), see Fig. 24.1 (mentioned as methylene dichloride)
- Trichloroethylene, at plant (Location: WEU), see Fig. 24.1
- Tetrachloroethylene, at plant (Location: WEU); see Fig. 24.1
- Methyl chloride, at regional storage (Location: CH); see Fig. 24.2
- Tetrachloroethylene, at regional storage (Location: CH); see Fig. 24.3

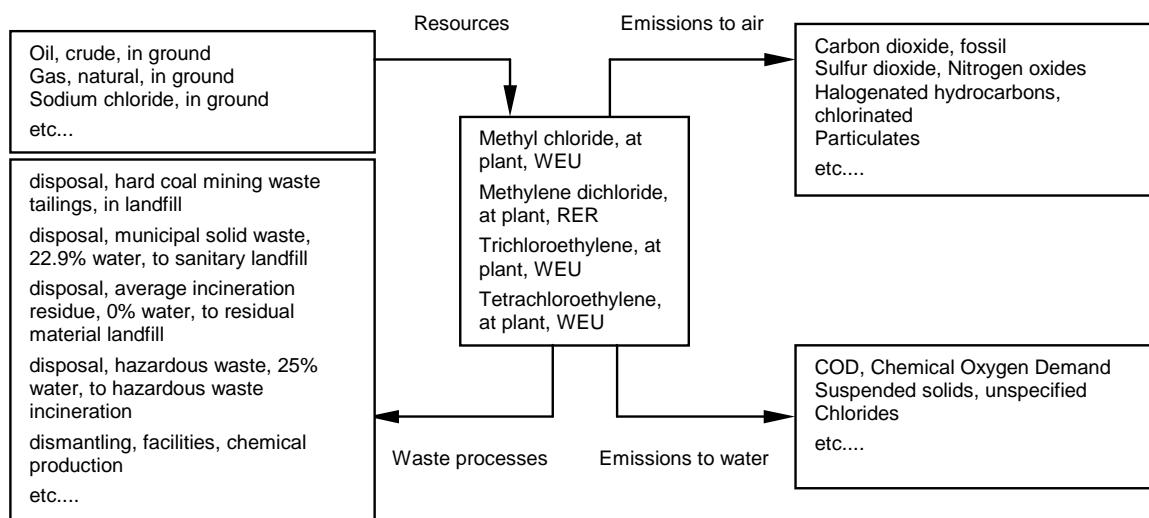


Fig. 24.1 Process chain for the production of methyl chloride, dichloromethane, trichloroethylene, and tetrachloroethylene

Processes at regional storage

To include the transport from the plant to a regional storehouse, which is representative for the use of tetrachloroethylene or methyl chloride in Switzerland, transport processes were included. With the distances from the relevant plant sites or production areas these transport processes were defined. The losses of product occurring within the transportation and storage were considered roughly.

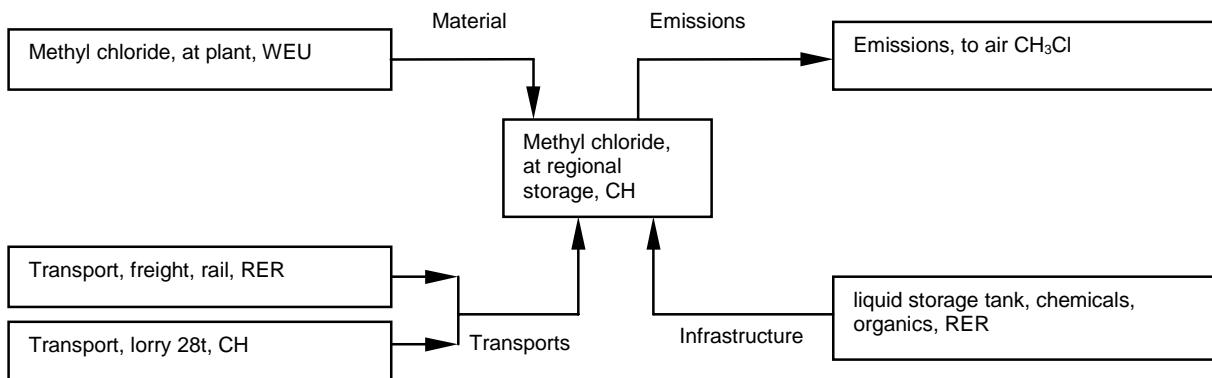


Fig. 24.2 Process chain for the process "methyl chloride, at regional storage"

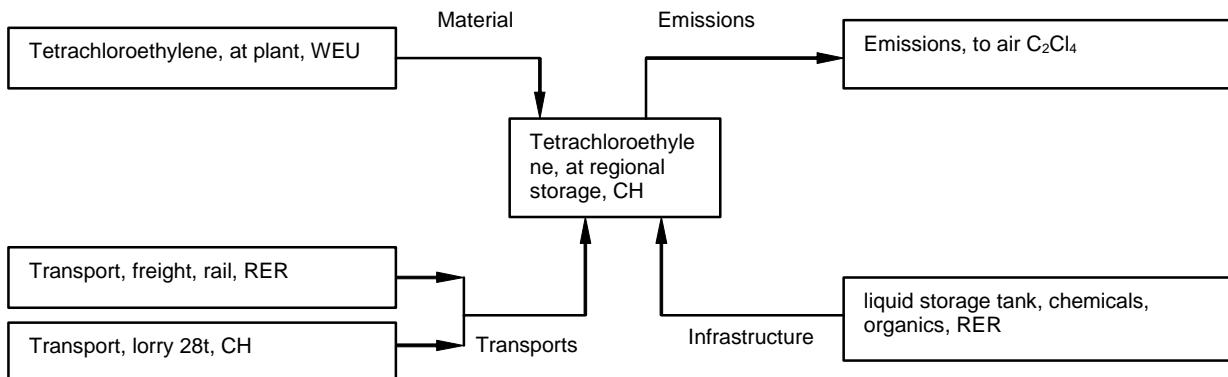
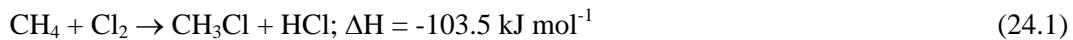


Fig. 24.3 Process chain for the process "tetrachloroethylene, at regional storage"

24.5 Methyl chloride, at plant

24.5.1 Production processes

A process scheme of methyl chloride production by methane chlorination is shown in Fig. 24.4. This production process can be described with the following equation:



Besides the production route with methane as carbon source also the production by methanol hydrochloration is common. This second process is shown in Fig. 24.5. This second production process can be described with the following equation:



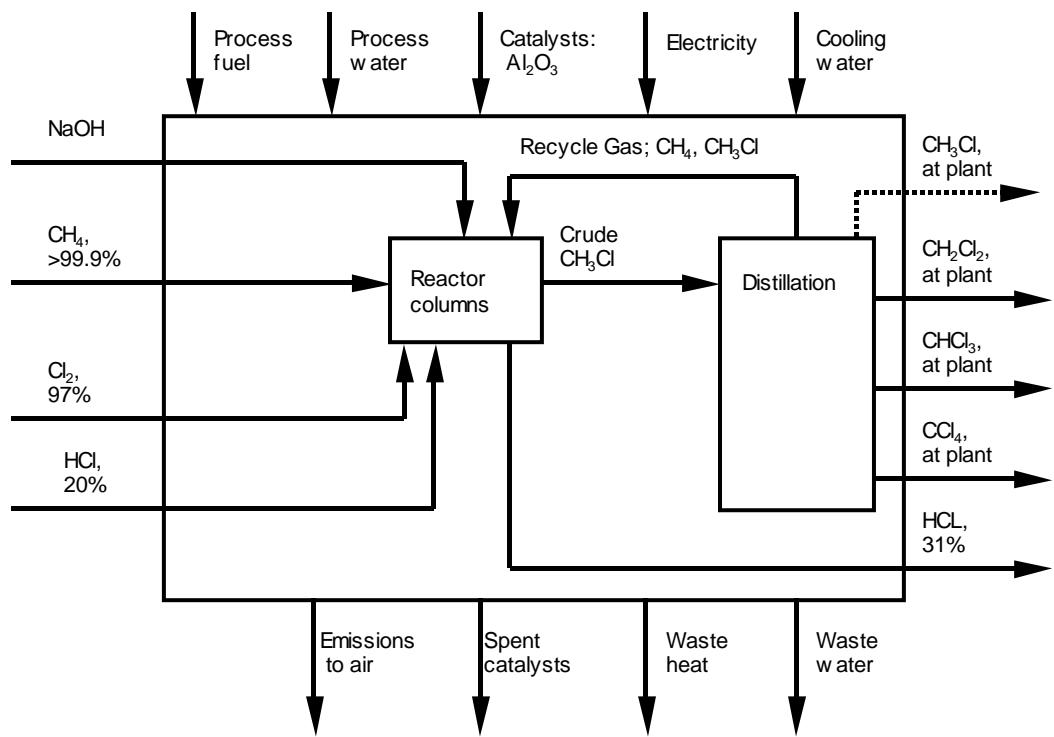


Fig. 24.4 Simplified process of methyl chloride production by methane chlorination

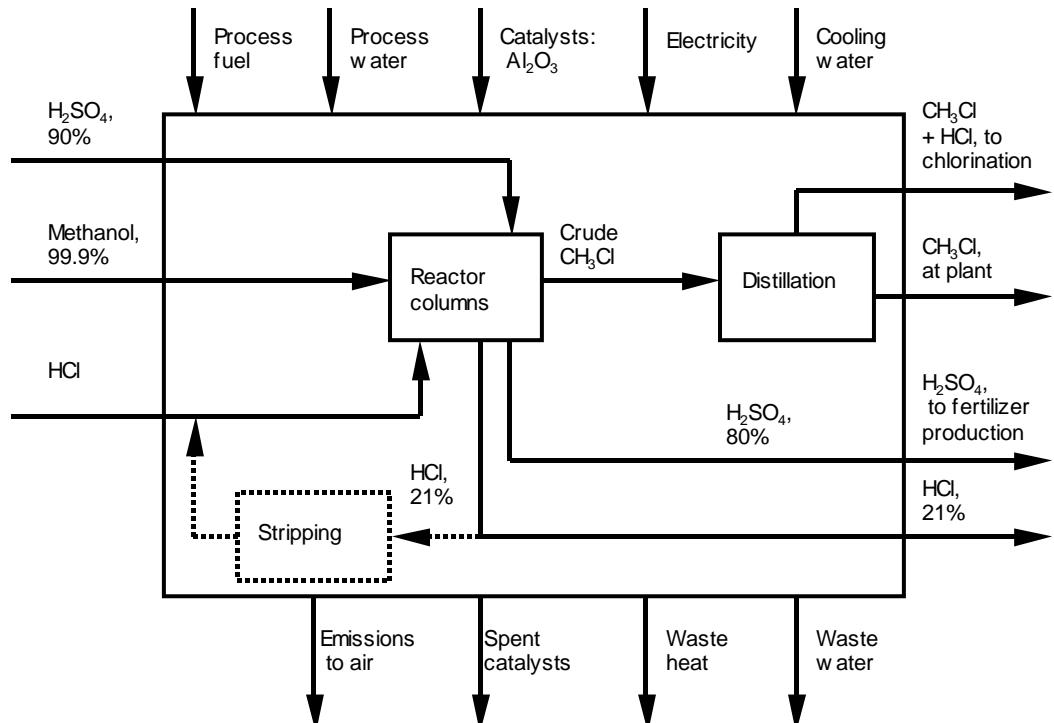


Fig. 24.5 Simplified process of methyl chloride production by methanol hydrochlorination

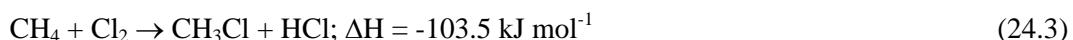
24.5.2 Inventory data

The process requirements and burdens were accounted according to the data of Boustead (1997b), which includes the production by methane chlorination and methanol hydrochloration. There was no information in those cumulated inventory data about the share of the two processes considered. Also the used allocation method to share the burdens between the obtained products in the methane chlorination process (methyl chloride, dichloromethane, chloroform, carbon tetrachloride) was unclear. These data were nevertheless used because it represents 78% of the annual European production of chloromethanes (Boustead (1997b)). The accounted data in the ecoinvent project are shown in Tab. 24.2 (resources and waste) and Tab. 24.3 (emissions to air and water).

24.6 Dichloromethane, at plant

24.6.1 Production process

The production of dichloromethane takes place by methane chlorination as shown in Fig. 24.4. Besides dichloromethane also methyl chloride, chloroform (trichloromethane) and carbon tetrachloride (tetrachloromethane) are obtained in this chlorination process. This production process can be described with the following equations:



24.6.2 Inventory data

The process requirements and burdens were accounted according to the data of Boustead (1997b). There was no information in those cumulated inventory data available about the used allocation method to share the burdens between the obtained products in the methane chlorination process (methyl chloride, dichloromethane, chloroform, carbon tetrachloride). These data were nevertheless used because it represents 78% of the annual European production of chloromethanes (Boustead (1997b)). The accounted data in the ecoinvent project are shown in Tab. 24.2 (resources and waste) and Tab. 24.3 (emissions to air and water).

24.7 Trichloroethylene, at plant

24.7.1 Production process

For the production of trichloroethylene either acetylene or ethylene is used as a feedstock. The acetylene route comprises acetylene chlorination to 1,1,2,2-tetrachloroethane followed by dehydrochlorination to trichloroethylene:



In the ethylene-based processes ethylene or ethylene based chlorohydrocarbons, preferably 1,2-dichloroethane, are chlorinated or oxochlorinated and dehydrochlorinated in the same reactor. Perchloroethylene is obtained as a byproduct in substantial amounts. More detailed information about this process route are in chapter 24.8 and Fig. 24.6.

24.7.2 Inventory data

The process requirements and burdens were accounted according to the data of Boustead (1997a). There was no information in those cumulated inventory data available about the used allocation method to share the burdens between the obtained products (tetrachloroethylene, trichloroethylene) in the ethylene-based process. Also no information was given to which amount the different production routes were used. These data were nevertheless used because it represents 90% of the annual European production of trichloroethylene (Boustead 1997a). The accounted data in the ecoinvent project are shown in Tab. 24.2 (resources and waste) and Tab. 24.3 (emissions to air and water).

24.8 Tetrachloroethylene, at plant

24.8.1 Production process

Tetrachloroethylene is produced by oxychlorination or chlorinolysis of raw materials such as propylene, 1,2-dichloroethane, chloropropenes and chloropropanes. It is mainly produced jointly with trichloroethylene by the so-called "TRI/PER" process. This process is based on chlorination or oxychlorination of the light fractions of residues from vinyl chloride monomer (VCM) manufacture. This production process can be described with the following equations:



Tetrachloroethylene can also be produced jointly with carbon tetrachloride in the "CTC/PER" process. This process known as chlorinolysis has been modified substantially to reduce the production of carbon tetrachloride. A disadvantage of the chlorinolysis is the net production of hydrogen chloride, which must be consumed by other processes. The production of methyl chloride production by oxychlorination is shown in Fig. 24.6 and the production by chlorinolysis in Fig. 24.7.

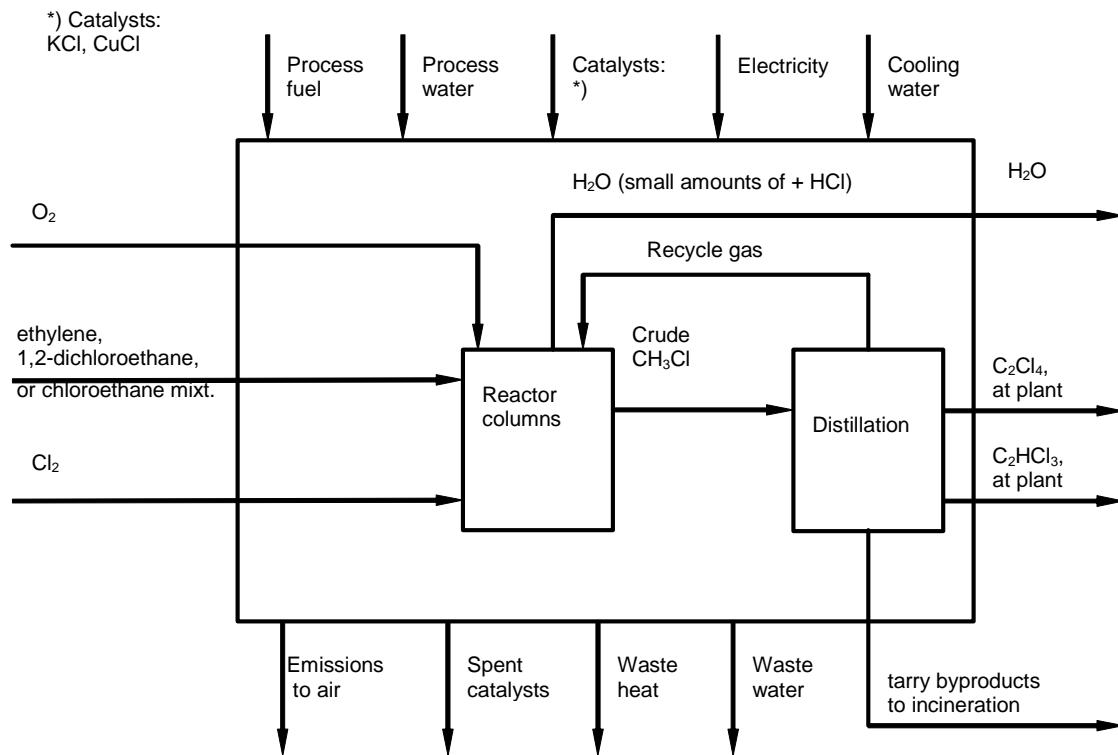


Fig. 24.6 Simplified process of tetrachloroethylene production by oxychlorination

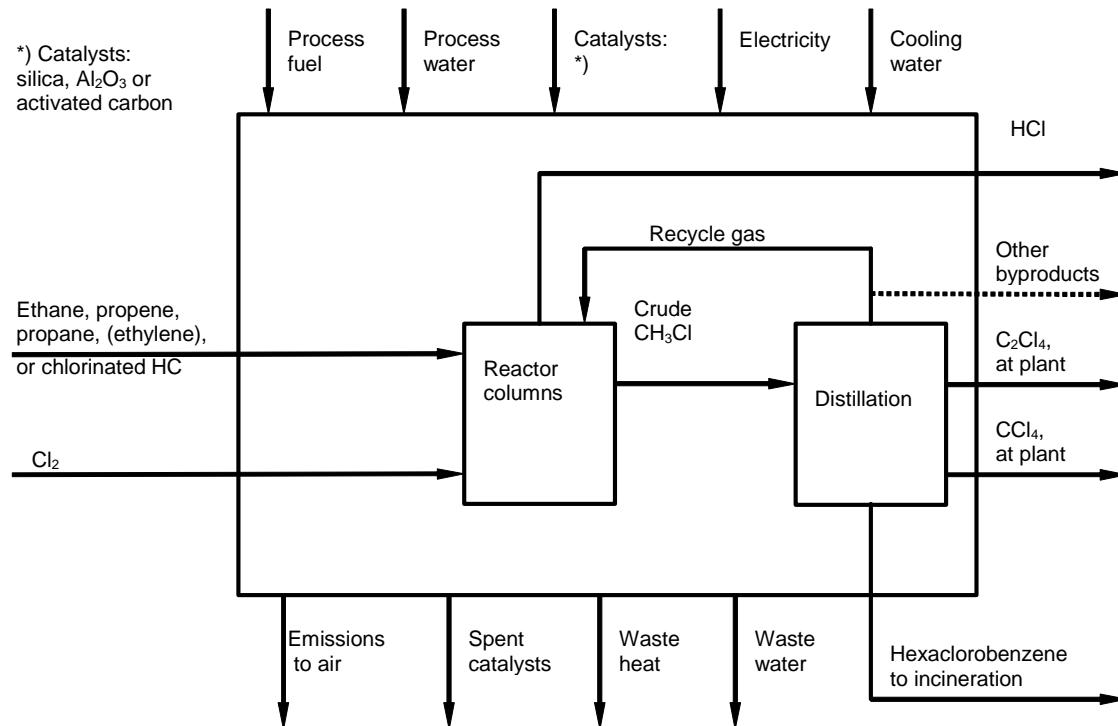


Fig. 24.7 Simplified process of tetrachloroethylene production by chlorinolysis

24.8.2 Inventory data

The process requirements and burdens were accounted according to the data of Boustead (1997a). There was no information in those cumulated inventory data available about the used allocation method to share the burdens between the obtained products (tetrachloroethylene, trichloroethylene) in the oxychlorination process. Also no information was given to which amount the different production routes were used. These data were nevertheless used because it represents 76% of the annual European production of tetrachloroethylene (Boustead (1997a)). The accounted data in the ecoinvent project are shown in Tab. 24.2 (resources and waste) and Tab. 24.3 (emissions to air and water).

Tab. 24.2 In- / Outputs for the modules “methyl chloride, at plant”, “dichloromethane, at plant”, “trichloroethylene, at plant” and “tetrachloroethylene, at plant”. Values for waste processes and resource use.

Process in- and output (per kg substance)	Unit	tetrachloroethylene, at plant, WEU	trichloroethylene, at plant, WEU	methylchloride, at plant, WEU	dichlormethane, at plant, RER
disposal, hard coal mining waste tailings, in surface backfill	kg	7.50E-02	1.20E-01	7.10E-02	7.70E-02
disposal, municipal solid waste, 22.9% water, to sanitary landfill	kg	3.10E-03	5.60E-03	1.60E-03	1.50E-03
disposal, average incineration residue, 0% water, to residual material landfill	kg	2.09E-02	2.61E-02	2.01E-02	2.71E-02
disposal, hazardous waste, 25% water, to hazardous waste incineration	kg	3.90E-03	6.10E-03	8.00E-04	8.40E-04
disposal, facilities, chemical production	kg	3.00E-05	2.40E-05	1.10E-05	7.00E-06
disposal, municipal solid waste, 22.9% water, to municipal incineration	kg	2.70E-05	1.80E-05	4.50E-06	2.50E-06
disposal, plastics, mixture, 15.3% water, to sanitary landfill	kg	2.00E-06	4.00E-06	5.00E-07	3.00E-06
disposal, wood untreated, 20% water, to sanitary landfill	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
Oil, crude, in ground	kg	1.80E-01	4.50E-01	7.70E-02	9.30E-02
Gas, natural, in ground	Nm3	3.63E-01	3.75E-01	8.38E-01	5.38E-01
Coal, hard, unspecified, in ground	kg	2.00E-01	4.00E-01	2.70E-01	2.80E-01
Coal, brown, in ground	kg	1.10E-01	6.00E-03	4.80E-02	3.70E-02
Peat, in ground	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Wood, unspecified, standing	m3	3.04E-09	3.04E-09	6.08E-09	1.82E-08
Energy, gross calorific value, in biomass	MJ	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Energy, potential, stock, in barrage water	MJ	2.70E-01	6.40E-01	1.80E-01	3.20E-01
Uranium, in ground	kg	6.66E-06	1.87E-05	1.03E-05	1.72E-05
Barite, 15% in crude ore, in ground	kg	0.00E+00	4.00E-04	6.50E-05	2.40E-04
Aluminum, 24% in bauxite, 11% in crude ore, in ground	kg	7.42E-05	1.01E-04	1.48E-05	1.11E-05
Clay, bentonite, in ground	kg	2.00E-05	9.00E-06	0.00E+00	0.00E+00
Anhydrite, in ground	kg	2.00E-06	0.00E+00	0.00E+00	0.00E+00
Chromium, 25.5 in chromite, 11.6% in crude ore, in ground	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Clay, unspecified, in ground	kg	5.00E-04	1.30E-03	0.00E+00	0.00E+00
Dolomite, in ground	kg	5.00E-06	5.00E-06	3.00E-06	2.00E-06
Feldspar, in ground	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Manganese, 35.7% in sedimentary deposit, 14.2% in crude ore, in ground	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Fluorspar, 92%, in ground	kg	2.00E-06	2.00E-06	2.00E-06	3.00E-06
Granite, in ground	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Gravel, in ground	kg	1.00E-06	2.00E-06	0.00E+00	0.00E+00
Iron, 46% in ore, 25% in crude ore, in ground	kg	4.00E-04	4.80E-04	2.10E-04	1.40E-04
Lead, 5%, in sulfide, Pb 2.97% and Zn 5.34% in crude ore, in ground	kg	0.00E+00	1.00E-06	1.00E-06	0.00E+00
Calcite, in ground	kg	7.80E-03	2.00E-02	5.50E-02	2.60E-02
Nickel, 1.98% in silicates, 1.04% in crude ore, in ground	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Olivine, in ground	kg	4.00E-06	4.00E-06	2.00E-06	1.00E-06
Phosphorus, 18% in apatite, 12% in crude ore, in ground	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sylvite, 25 % in sylvite, in ground	kg	3.00E-06	3.00E-06	0.00E+00	0.00E+00
Rutile, in ground	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sand, unspecified, in ground	kg	7.20E-02	1.90E-01	3.30E-04	6.80E-04
Shale, in ground	kg	6.00E-06	3.00E-06	0.00E+00	0.00E+00
Sodium chloride, in ground	kg	1.20E+00	1.90E+00	9.90E-01	1.20E+00
Sulfur, in ground	m3	1.00E-03	7.30E-04	4.20E-03	1.10E-03
Water, unspecified natural origin	m3	8.20E-03	6.81E-03	3.91E-03	4.91E-03
Water, river	m3	4.20E-06	1.00E-05	3.90E-06	4.10E-06
Water, salt, ocean	m3	3.50E-06	6.60E-06	2.30E-07	1.50E-07
Water, well, in ground	m3	3.00E-07	1.10E-03	1.90E-04	7.10E-04
Water, cooling, unspecified natural origin	m3	1.10E-01	4.40E-02	2.00E-02	2.40E-02

Tab. 24.3 In- / Outputs for the modules “methyl chloride, at plant”, “dichloromethane, at plant”, “trichloroethylene, at plant”, and “tetrachloroethylene, at plant”. Values for emissions to air and water.

Process in- and output (per kg substance)		tetrachloroethylene, at plant, WEU	trichloroethylene, at plant, WEU	methylchloride, at plant, WEU	dichlormethane, at plant, RER	
	Unit	Value	Value	Value	Value	
Emissions, to air	Particulates, > 10 um	kg	1.34E-03	1.79E-03	1.60E-03	1.60E-03
	Particulates, > 2.5 um, and < 10um	kg	1.81E-03	2.41E-03	2.15E-03	2.15E-03
	Particulates, < 2.5 um	kg	1.05E-03	1.40E-03	1.25E-03	1.25E-03
	Carbon monoxide, fossil	kg	3.80E-03	0.00E+00	1.20E-03	1.00E-03
	Carbon dioxide, fossil	kg	2.00E+00	0.00E+00	2.40E+00	2.30E+00
	Sulfur dioxide	kg	9.40E-03	2.40E-02	1.20E-02	1.30E-02
	Nitrogen oxides	kg	8.80E-03	1.20E-02	1.30E-02	1.40E-02
	Dinitrogen monoxide	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	NM VOC, non-methane volatile organic compounds, unspecified origin	kg	1.88E-03	3.99E-03	1.73E-03	1.06E-03
	Methane, fossil	kg	7.40E-03	0.00E+00	2.00E-02	1.40E-02
	Hydrogen sulfid	kg	5.00E-07	1.00E-06	5.00E-07	5.00E-07
	Hydrogen chloride	kg	1.10E-04	2.50E-04	2.20E-04	1.80E-04
	Chlorine	kg	2.00E-06	5.00E-07	5.00E-07	2.00E-06
	Hydrogen fluoride	kg	5.00E-06	1.00E-05	7.00E-06	7.00E-06
	Lead	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Fluorine	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Halogenated hydrocarbons, chlorinated	kg	2.40E-03	5.20E-03	7.80E-04	3.40E-03
	Hydrocarbons, aromatic	kg	2.00E-06	5.00E-06	5.00E-07	5.00E-07
	Hydrocarbons, aliphatic, alkanes, cyclic	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Methane, dichlorodifluoro-, CFC-12	kg	1.50E-04	4.00E-05	1.20E-05	6.70E-05
	Aldehydes, unspecified	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Cyanide	kg	0.00E+00	5.00E-07	0.00E+00	0.00E+00
	Sulfate	kg	4.90E-07	4.90E-07	4.90E-06	4.90E-07
	Hydrogen	kg	5.60E-04	2.70E-04	2.20E-03	8.00E-04
	Mercury	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Ammonia	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Carbon disulfide	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Ethane, 1,2-dichloro-	kg	5.50E-03	1.40E-02	6.00E-06	2.00E-06
	Ethene, chloro-	kg	2.80E-03	7.40E-03	6.00E-06	2.00E-06
	Heat, waste	MJ	2.64E+01	0.00E+00	3.57E+01	3.89E+01
Emissions, to water	COD, Chemical Oxygen Demand	kg	4.80E-04	6.50E-04	1.90E-04	1.40E-04
	BOD5, Biological Oxygen Demand	kg	4.20E-05	1.40E-04	1.30E-05	8.00E-06
	Acidity, unspecified	kg	2.90E-05	6.60E-05	3.30E-05	2.00E-05
	Solved solids	kg	8.20E-05	1.30E-04	2.80E-05	2.60E-05
	Hydrocarbons, unspecified	kg	4.40E-05	3.90E-05	8.85E-05	3.25E-05
	Ammonium, ion	kg	2.00E-06	4.00E-06	1.00E-06	1.00E-06
	Suspended solids, unspecified	kg	1.20E-03	2.90E-03	5.20E-04	1.00E-03
	Phenol	kg	3.00E-06	1.10E-05	5.00E-07	4.00E-06
	Aluminum	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Calcium, ion	kg	1.20E-03	3.30E-03	1.60E-02	6.10E-03
	Copper, ion	kg	5.00E-07	1.00E-06	5.00E-07	5.00E-07
	Iron, ion	kg	1.90E-04	4.00E-06	3.80E-05	1.10E-05
	Mercury	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Lead	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Magnesium	kg	9.00E-06	5.00E-07	6.00E-06	8.00E-06
	Sodium, ion	kg	9.70E-02	2.30E-01	1.00E-01	1.10E-01
	Potassium, ion	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Nickel, ion	kg	5.00E-07	1.00E-06	5.00E-07	5.00E-07
	Zinc, ion	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Nitrate	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Nitrogen	kg	2.00E-06	5.00E-07	1.00E-06	5.00E-07
	Chromium VI	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Chloride	kg	1.60E-01	3.60E-01	1.90E-01	1.90E-01
	Cyanide	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Fluoride	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Sulfate	kg	8.20E-04	2.00E-04	1.40E-03	3.90E-03
	Carbonate	kg	1.80E-05	8.00E-06	2.00E-06	5.00E-07
	Phosphorus	kg	8.80E-07	2.20E-07	8.80E-07	2.20E-07
	Arsenic, ion	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Ethane, 1,2-dichloro-	kg	1.50E-05	4.10E-05	5.00E-07	5.00E-07
	Ethene, chloro-	kg	0.00E+00	0.00E+00	5.00E-07	5.00E-07
	Oils, unspecified	kg	2.80E-05	7.30E-05	5.00E-07	5.00E-07
	Chlorine	kg	3.90E-05	1.00E-04	5.00E-07	5.00E-07
	Chlorinated solvents, unspecified	kg	3.40E-05	1.20E-04	3.00E-05	7.50E-05
	Sulfide	kg	1.60E-05	4.20E-05	1.80E-05	1.80E-05
	Bromate	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	Chlorate	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	AOX, Adsorbable Organic Halogen as Cl	kg	5.00E-07	5.00E-07	5.00E-07	5.00E-07
	TOC, Total Organic Carbon	kg	1.50E-04	3.00E-06	2.20E-05	6.00E-06

24.9 Methyl chloride / Tetrachloroethylene, at regional storage

24.9.1 Transportation to regional store

There is no production of methyl chloride and tetrachloroethylene in Switzerland. According to the plant sites presented in (Wells (1991)) the distances to a regional storage in Switzerland were estimated as similar to the standard distances used for other organic base chemicals. This leads to a transport requirement of 600 km rail transport and 50 km road transport. The products are transported in vessels made of iron and steel. For high purity products also tanks made of stainless steel are used. Under normal atmospheric pressure methyl chloride is gaseous. Therefore, tanks for the transport and storage of larger quantities of methyl chloride are pressurised (1.3 MPa working pressure) to store the

product as liquid. The selected values for distribution of methyl chloride and tetrachloroethylene to regional storage in Switzerland are given in Tab. 24.4.

24.9.2 Product losses during transportation and storage

Strict specifications with respect to safety are applied for storage and transport of chlorinated hydrocarbons to prevent spillage and overfilling. There were no data on the average emission of methyl chloride or tetrachloroethylene during transport and storage processes. As an approximation data given in EPA 1984 for the emissions during handling and storage of chloroform in a product tank was applied for the methyl chloride and the tetrachloroethylene inventory. As emission control it was assumed that a refrigerated condenser is used to recycle 87% of the emissions back to the tank. The emissions after control presented in (EPA (1984)) are 0.11 g per kg product for the tank storage (1500 m^3) and 0.046 g per kg product for the handling, which includes loading of tank cars for transport. As a total emission 0.16 g per kg product throughput was applied for the emissions of methyl chloride and tetrachloroethylene during storage and transport. This emission factor is only an approximation to roughly include the emissions occurring. The emissions were accounted as emissions to air.

24.9.3 Infrastructure

The infrastructure for the regional storage of methyl chloride and tetrachloroethylene was approximated with the process “liquid storage tank, chemicals, organics”. This infrastructure module represent a tank farm (4 tanks) with a total storage capacity of $16'000 \text{ m}^3$. The storage tanks used for methyl chloride and tetrachloroethylene will be of smaller size than the assessed and the material demand higher due to higher requirements on safety and pressure resistance. Nevertheless this module was used as an approximation of the infrastructure for storage. To calculate the infrastructure demand a lifetime of 50 years with an average storage time of two month was assumed for the storage tanks. This leads to an amount of $4.8 * 10^6 \text{ m}^3$ stored during the lifetime of the storage tanks. Applying the densities stated in Tab. 24.1, this leads to 4.4 Mt methyl chloride and 7.8 Mt tetrachloroethylene stored. Thereof an amount of $0.23 * 10^9$ units of the infrastructure module was calculated per kg methyl chloride and $0.13 * 10^9$ units per kg tetrachloroethylene.

Tab. 24.4 Average needed transportation for distribution of 1 kg methyl chloride or tetrachloroethylene to regional storage in Switzerland

Process	Unit	1 kg methyl chloride, at regional storage	1 kg tetrachloroethylene, at regional storage
Tetrachloroethylene, at plant	kg	-	1
Methyl chloride, at plant	kg	1	-
Transport, freight, rail, RER	tkm	0.6	0.6
Transport, lorry 28t, CH	tkm	0.05	0.05
Liquid storage tank, chemicals, organics, RER	unit	$0.23 * 10^{-9}$	$0.13 * 10^{-9}$
Methane, monochloro-, to air	kg	$0.16 * 10^{-3}$	-
Ethene, tetrachloro-, to air	kg	-	$0.16 * 10^{-3}$

24.10 Data quality considerations

There was no uncertainty assessment applied for the cumulated product system inventory data derived from Boustead (1997b) and Boustead (1997a) for the inventories “methyl chloride, at plant”, “dichloromethane, at plant” and “tetrachloroethylene, at plant”. This does not represent the reality of

those data but there was no appropriate way to include any uncertainty for those system inventory data.

For the data of the modules “methyl chloride, at regional storage” presented in Tab. 37.4 and “tetrachloroethylene, at regional storage” presented in Tab. 24.6 data uncertainty lies within the distances and the modal split applied for the transportation from the production plant to the regional storage in Switzerland. The uncertainty of the applied emissions for handling and storage are high because of the use of aged data from trichloromethane production (chloroform). The included infrastructure is approximated with a module describing storage tanks as used for methanol or fuels. Therefore, there is high uncertainty about the values used.

Tab. 24.5 In- / Outputs for the module “methyl chloride, at regional storage”, location CH

Process output: 1 kg, methylchloride, at regional storage, CH						
Name, Location	Value	Unit	Uncertainty			Comment
			Type	Score	St.Dev.	
methylchloride, at plant, WEU	1.00E+0	kg	lognorm	1,1,1,1,1,1	1.05	Material input, no additional uncertainty
liquid storage tank, chemicals, organics, CH	2.30E-10	unit	lognorm	4,5,1,5,5,5	3.82	Estimated, Proxy used
transport, lorry 28t, CH	6.00E-1	tkm	lognorm	4,5,1,2,1,5	2.14	Estimate of distances from European production
transport, freight, rail, RER	5.00E-2	tkm	lognorm	4,5,1,2,1,5	2.14	Estimate of distances from European production
(2) Methane, monochloro-, air, high population density	1.60E-4	kg	lognorm	2,5,5,3,4,5	2.55	Aged data from chloroform production
1) from technosphere; 2) Emissions to air						

Tab. 24.6 In- / Outputs for the module tetrachloroethylene, at regional storage”, location CH

Process output: 1 kg, tetrachloroethylene, at regional storage, CH						
Name, Location	Value	Unit	Uncertainty			Comment
			Type	Score	St.Dev.	
tetrachloroethylene, at plant, WEU	1.00E+0	kg	lognorm	1,1,1,1,1,1	1.05	Material input, no additional uncertainty
liquid storage tank, chemicals, organics, CH	1.30E-10	unit	lognorm	4,5,1,5,5,5	3.82	Estimated, Proxy used
transport, lorry 28t, CH	6.00E-1	tkm	lognorm	4,5,1,2,1,5	2.14	Estimate of distances from European production
transport, freight, rail, RER	5.00E-2	tkm	lognorm	4,5,1,2,1,5	2.14	Estimate of distances from European production
(2) Ethene, tetrachloro-, air, high population density	1.60E-4	kg	lognorm	2,5,5,3,4,5	2.55	Aged data from chloroform production
1) from technosphere; 2) Emissions to air						

24.11 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

24.12 Conclusions

The inventory data used in these processes does not give transparency on the processes used and allocations made because the data used were cumulated. Therefore, many emissions especially soil emissions are not accounted. Further problems arise because sum parameters are included (as e.g. “metals, unspecified” or “CFC/HCFC”) which give large uncertainties in the interpretation of the data. Because of the cumulated data also no land occupation and land transformation could be included in the dataset. This leads to an incompleteness of the dataset, which has to be considered when using it. Also the uncertainty of the data used could not be determined for those datasets. Nevertheless the data refers on a large share of the European production and should therefore be representative for the production of those chemicals.

For future work on this inventories the data should be split into the different process steps (as e.g. production of methane, chlorine, methanol) to achieve a more transparent inventory where also the inclusion of the land use and uncertainty assessments are possible.

24.13 References

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25 Chloromethyl methyl ether

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 Review: Roland Hischier, EMPA St. Gallen

25.1 Introduction

Chloromethyl methyl ether (C_2H_5ClO , CAS-No. 107-30-2, synonyms: CMME, Chlorodimethyl ether, Chlordinmethylether, Dimethylchloroether, chloromethoxymethane, Methyl chloromethyl ether; Mono-chlorodimethyl ether, Methoxymethyl chloride, HSDB 908) is a colourless volatile liquid with a characteristic odour.

Technical grade chloromethyl methyl ether (CMME) contains from 1 to 8% bis-chloromethyl ether (BCME). The vapour pressure and water solubility of these compounds are high and the log octanol/water partition coefficients ($\log K_{OW}$) are low. CMME is rapidly hydrolysed by water. The Half-life (at 25°C) in water is stated to be <0.007 s and in air 3.5 to 6 min. Because of the highly reactive nature of CMME in water and air, this alpha-chloroalkyl ether is not expected to be present in the environment. Chloromethyl methyl ether is a proven human carcinogen, mainly because of its content of BCME (impurity in technical grade CMME). It also causes chromosomal aberrations in occupationally exposed workers Liteplo & Gomes 1998.

For this inventory the functional unit is 1 kg of anhydrous chloromethyl methyl ether. The most important chemical and physical properties of chloromethyl methyl ether used in this inventory are given in Fig. 25.1.

Tab. 25.1 Chemical and physical properties of chloromethyl methyl ether

Property	Unit	Value	Remarks
Molecular weight	$g\ mol^{-1}$	80.51	
Specific gravity	$kg\ m^{-3}$	1060	at room temperature
Boiling point	°C	59	at normal pressure

25.2 Reserves and Resources of material

There was no actual information on commercial production of chloromethyl methyl ether (CMME) available. Also, no information was available on the amounts of CMME produced within Europe.

According to Liteplo & Gomes 1998 chloromethyl methyl ether (CMME) is produced by the reaction of anhydrous hydrogen chloride, methanol, and formaldehyde or by the direct chlorination of dimethyl ether. An additional method, which is designed to produce CMME that is free of BCME impurities, involves the addition of actinium chloride to a slight excess of anhydrous dimethoxymethane at room temperature. There was no information available on the actual used process for commercial production of CMME. For this inventory a production from anhydrous hydrogen chloride, methanol and formaldehyde as described by Fishbein L. 1979 was assumed.

25.3 Use of material / product

According to Liteplo & Gomes 1998 chloromethyl methyl ether is used in the synthesis of chloromethylated compounds, as an alkylating agent, and as solvent in the manufacture of water repellents. Chloromethyl methyl ether is also used in the production of ion-exchange resins and industrial polymers.

25.4 Systems characterization

In the production process for chloromethyl methyl ether, the main raw materials, an approximation of the production energy, and estimations for the emissions to water and air were considered. This module represents only a rough estimation of the process requirements and should only be used for processes where the impact of chloromethyl methyl ether is not considered to be high.

For this inventory the functional unit is 1 kg chloromethyl methyl ether (anhydrous). As process location, Europe (RER) was used. The process chain was assessed as shown in Fig. 25.1. For the neutralisation of the unreacted hydrogen chloride in the wastewater a stoichiometric amount of sodium hydroxide was assumed to be used in the process.

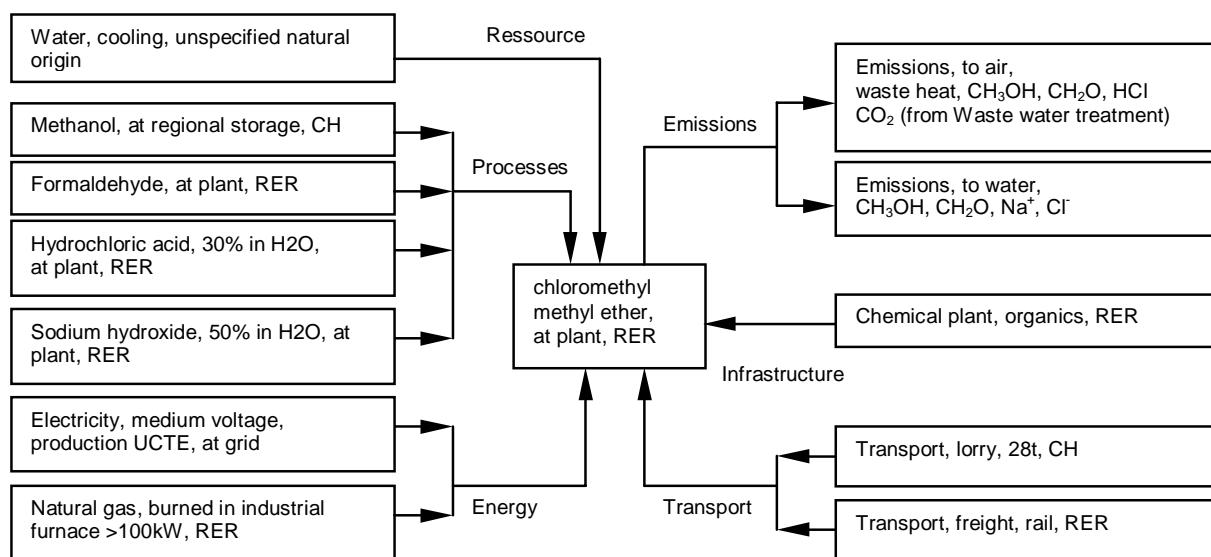


Fig. 25.1 Process chain for the production of chloromethyl methyl ether

25.5 Chloromethyl methyl ether, at plant (location: RER)

25.5.1 Process

Due to missing production data, this inventory about the production process for chloromethyl methyl ether bases on stoichiometric calculations. In the calculations a process yield of 95% for the used chemicals was assumed. The emissions to air and water were estimated using mass balances. It was assumed that the wastewater is treated in an internal wastewater treatment plant. To estimate the process energy demand, these values were approximated with data from a large chemical plant (Gendorf 2000). Due to these approximations the uncertainty within the results of this inventory is large.

For this inventory a production process containing a reaction step and a distillation was assumed. No information was available on catalysts or further process steps needed for the production of chloromethyl methyl ether. The assumed production process scheme from methanol, hydrogen chloride and formaldehyde is shown in Fig. 25.2. The overall reaction for the production of chloromethyl methyl ether can be formulated as follows:



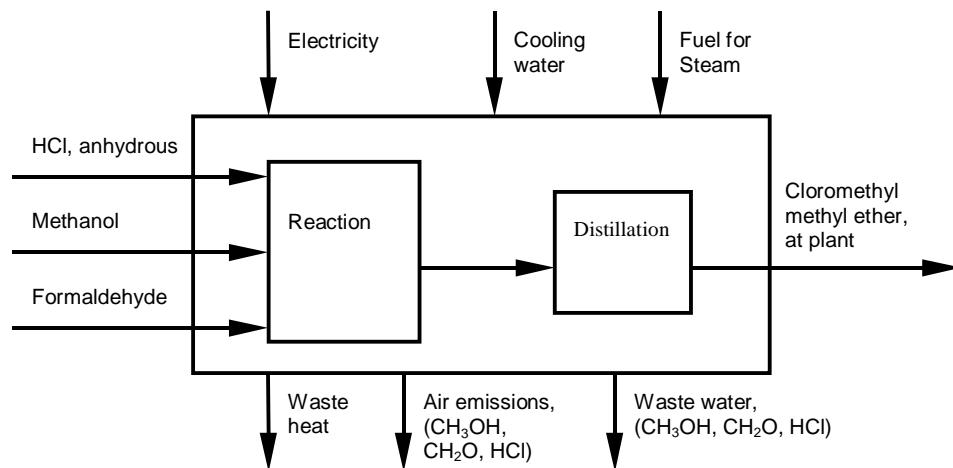


Fig. 25.2 Simplified process for the production of chloromethyl methyl ether

25.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the wastewater treatment. Fossil fuel is needed to generate the desired heat for the preheating and the distillation of the product. There was no information available on the amount of energy used for the production process. These values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf 2000). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the chloromethyl methyl ether production. This total energy demand was covered with natural gas (50%), electricity (38%) and steam from external energy sources (12%). For this inventory all energy used for heat or steam was assumed to be natural gas. An amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was assumed. A summary of the values used is given in Tab. 25.2.

Raw materials and chemicals

For the production of 1 kg chloromethyl methyl ether (CMME) the following stoichiometric inputs are needed (yield 100%):

- Methanol, CH₃OH: 0.398 kg (12.4 mol)
- Hydrogen chloride (anhydrous), HCl: 0.452 kg (12.4 mol)
- Formaldehyde, CH₂O: 0.373 kg (12.4 mol)

For the calculation a production yield of 95% was used. To produce 1 kg CMME therefore 0.419 kg methanol, 0.477 kg hydrogen chloride and 0.393 kg formaldehyde were considered as raw materials in this inventory. For hydrochloric acid there was no process available for anhydrous HCl. As an approximation the process data of a 30% HCl solution was used. For the neutralisation of the unreacted hydrogen chloride in the wastewater a stoichiometric amount of sodium hydroxide was assumed to be used in the process. This leads to a demand of 25.1 g NaOH (0.63 mol) per kg CMME in order to neutralise 22.9 g HCl in the wastewater. The stoichiometric output of water (0.224 kg per kg CMME) from the process was not considered as co-product. This water was assumed to be disposed with the other wastewater of the process. A summary of the values used is given in Tab. 25.2.

Water use

There was no information available on the amount of cooling water used within the plant. The process cooling water demand was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf 2000). In this plant an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the chloromethyl methyl ether production. According to IPPC 2000 the cooling water demand may reach 86 kg kWh⁻¹ for an once through cooling system, which would lead to a cooling water demand of 48 kg per kg CMME for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m³ cooling water per kg CMME was used.

Transport

For methanol a process, which includes transports to a regional storage, was used and therefore no further transport requirements were considered for this raw material. For the transportation of the other materials the standard distances were applied. A distance of 200 km rail and 100 km road was considered for the amount of 0.48 kg HCl (anhydrous HCl). A distance of 600 km rail and 100 km road was assumed for an amount of 0.39 kg formaldehyde and 0.05 kg NaOH (including 50 % H₂O). These values sum up to of 0.361 tkm rail transport and 0.092 tkm road transport (lorry 28 t) per kg CMME.

25.5.3 Emissions

Waste heat

It was assumed that 100% of the electricity consumed (1.2 MJ per kg chloromethyl methyl ether) is converted to waste heat and released to the air.

Emissions to air

There was no data available on process emissions to air for the production of chloromethyl methyl ether. As approximation the air emissions were estimated to be 0.2% of the raw material input. No emissions of chloromethyl methyl ether to the air were accounted because CMME is usually produced in closed system operations and will hydrolyse within a few minutes to methanol, formaldehyde, and HCl because of the air humidity. These assumptions lead to air emissions of 0.84 g methanol, 0.79 g formaldehyde and 0.95 g HCl per kg CMME.

Emissions to water

The remaining amounts of unreacted raw materials were assumed to leave the production process with the wastewater. This assumption leads to a pollution of the wastewater with 20.1 g methanol, 18.8 g formaldehyde and 22.9 g HCl per kg CMME. Further, it was assumed that this wastewater is treated in an internal wastewater plant. The removal efficiency of the wastewater treatment plant was estimated with data from different effluent treatment plants operated within the chemical sector in the EU (IPPC 2002). The removal efficiency for methanol and formaldehyde was assumed to be 90% leading to emissions of 2.01 g methanol and 1.88 g formaldehyde per kg product in the treated water. The carbon contained in the removed methanol and formaldehyde was accounted as CO₂ emissions to air (49.7 g CO₂ per kg product). The hydrogen chloride in the wastewater (22.9 g or 0.63 mol) was assumed to be neutralised with sodium hydroxide leading to an emission of 22.2 g Cl⁻ and 14.4 g Na⁺ to the surface water (river). The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amounts of methanol and formaldehyde in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst-case scenario BOD = COD and TOC = DOC was used.

No emissions of chloromethyl methyl ether to water were accounted because it will hydrolyze instantaneously in water to the reaction products methanol, formaldehyde, and HCl. A summary of the values used in this inventory is given in Tab. 25.2.

Solid wastes

Solid wastes generated during the production of chloromethyl methyl ether such as spent catalysts were neglected in this inventory.

Tab. 25.2 Energy demand, resource demand and emissions for the production of chloromethyl methyl ether.

Resources, emissions	Unit	Value per kg chloromethyl methyl ether	Remarks
Methanol, at regional storage	kg	0.419	Stoichiometric calc., 95% yield
Hydrochloric acid, 30% in H ₂ O, at plant; ¹	kg	0.477	Stoichiometric calc., 95% yield
Formaldehyde, at plant	kg	0.393	Stoichiometric calc., 95% yield
Electricity, medium voltage, at grid; ²	kWh	0.333	Estimation
Natural gas, burned in industrial furnace >100kW; ²	MJ	2	Estimation
Water, cooling, unspecified; ²	kg	24	Estimation
Waste heat, to air	MJ	1.2	Calculated from electricity demand
Methanol (CH ₃ OH), to air	kg	0.84 * 10 ⁻³	Estimated as 0.2% of the input
Formaldehyde (CH ₂ O), to air	kg	0.79 * 10 ⁻³	Estimated as 0.2% of the input
Hydrogen chloride (HCl), to air	kg	0.95 * 10 ⁻³	Estimated as 0.2% of the input
CO ₂ , to air; ³	kg	74.6 * 10 ⁻³	From waste water treatment
Methanol (CH ₃ OH), to water; ³	kg	2.01 * 10 ⁻³	Calculated from mass balance
Formaldehyde (CH ₂ O), to water; ³	kg	1.88 * 10 ⁻³	Calculated from mass balance
Chloride, Cl ⁻ ; ³	kg	22.2 * 10 ⁻³	Calculated from mass balance
Sodium, Na ⁺ ; ³	kg	14.4 * 10 ⁻³	Stoichiometric calculation
COD, BOD; ⁴	kg	4.82 * 10 ⁻³	Calculated from water emissions
DOC, TOC; ⁴	kg	1.51 * 10 ⁻³	Calculated from water emissions
Transport, lorry, 28t	tkm	0.092	Calculated with standard distances
Transport, freight, rail	tkm	0.361	Calculated with standard distances
Chemical plant, organics	Unit	4 * 10 ⁻¹⁰	Approximation for infrastructure

¹ Process approximation for anhydrous hydrogen chloride

² Approximated with data from a large chemical plant site in Germany (Gendorf 2000).

³ 4.8% of input is assumed to be emitted to a wastewater treatment plant with an efficiency of 90% for C. Eliminated C is emitted as CO₂ to air. HCl in wastewater is neutralised with NaOH leading to Cl⁻ and Na⁺ emissions to water.

⁴ Calculated from methanol and formaldehyde emissions using worst case scenario COD = BOD, DOC = TOC

25.5.4 Infrastructure

No information was available on the infrastructure of the production plant. It was assumed that the importance of infrastructure is low and therefore the module “chemical plant, organics” was used as ap-

proximation. For this module with a production capacity of 50'000 t per year and a plant lifetime of 50 years, an amount of $4 * 10^{-10}$ units per kg chloromethyl methyl ether was included.

25.6 Data quality considerations

Tab. 25.3 shows the data quality indicators for the inventory of chloromethyl methyl ether production (location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the chloromethyl methyl ether production has a high uncertainty, because only few data were available. Therefore, the data for the used materials were assessed with stoichiometric calculations and the energy demand was extrapolated from an average chemical process. The highest uncertainties origin from the process path itself, because the production process may not be similar to the process used here. This is considered in the uncertainty score “further technological correlation”. Moreover, the process energy demand and the emissions base mainly on assumptions and approximations due to missing data. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Also for the infrastructure only an approximation was used because of missing data.

Tab. 25.3 In- / outputs for the module “chloromethyl methyl ether, at plant”, location GLO

Process output: 1 kg, trimethylamine, at plant, RER		Value	Unit	Uncertainty			Comment
Name, Location	Type	Score	St.Dev.				
methanol, at regional storage, CH	1.71E+0	kg	lognorm	4,nA,nA,nA,nA,nA	1.21		Stoichiometric calculation (95% yield)
ammonia, liquid, at regional storehouse, RER	3.03E-1	kg	lognorm	4,nA,nA,nA,nA,nA	1.21		Stoichiometric calculation (95% yield)
electricity, medium voltage, production UCTE, at grid, UCTE	3.33E-1	kWh	lognorm	5.5,1,1,4,5	1.88		Approximation with data of a large chem. plant
natural gas, burned in industrial furnace >100kW, RER	2.00E+0	MJ	lognorm	5.5,1,1,4,5	1.88		Approximation with data of a large chem. plant
chemical plant, organics, RER	4.00E-10	unit	lognorm	5.5,1,1,4,5	3.55		Approximation with average chem. plant
Water, cooling, unspecified natural origin	2.40E-2	m3	lognorm	5.5,1,1,4,5	1.88		Approximation with data of a large chem. Plant
Heat, waste, to air, high population density	1.20E+0	MJ	lognorm	5.5,1,1,4,5	1.88		Calculated from electricity demand
Methanol, to air, high population density	3.42E-3	kg	lognorm	5.5,nA,nA,nA,5	2.32		Estimated
Ammonia, to air, high population density	6.07E-4	kg	lognorm	5.5,nA,nA,nA,5	2.32		Estimated
Carbon dioxide, fossil, to air, high population density	1.02E-1	kg	lognorm	5.5,nA,nA,4,5	1.88		Estimated from mass balance and WWTP effic.
BOD5, Biological Oxygen Demand, to water, river	9.73E-3	kg	lognorm	5.5,nA,nA,4,5	2.11		Estimated from mass balance and WWTP effic.
COD, Chemical Oxygen Demand, to water, river	9.73E-3	kg	lognorm	5.5,nA,nA,4,5	2.11		Estimated from mass balance and WWTP effic.
DOC, Dissolved Organic Carbon, to water, river	3.08E-3	kg	lognorm	5.5,nA,nA,4,5	2.11		Estimated from mass balance and WWTP effic.
TOC, Total Organic Carbon, to water, river	3.08E-3	kg	lognorm	5.5,nA,nA,4,5	2.11		Estimated from mass balance and WWTP effic.
Methanol, to water, river	8.22E-3	kg	lognorm	5.5,nA,nA,4,5	3.55		Estimated from mass balance and WWTP effic.
Ammonium, ion, to water, river	4.63E-3	kg	lognorm	5.5,nA,nA,4,5	2.11		Estimated from mass balance and WWTP effic.
Nitrate, to water, river	1.06E-2	kg	lognorm	5.5,nA,nA,4,5	2.11		Estimated from mass balance and WWTP effic.

1) From technosphere, 2) Resources

nA = not applicable

25.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

25.8 Conclusions

The quality of the inventory for chloromethyl methyl ether production depends strongly on the data used for the emissions and the yield. Also data concerning the commercially used process path is missing. For further work on this inventory these data should be improved by using data from specific plants within Europe. This would also improve the data used for energy consumption and infrastructure.

25.9 References

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26 Chromium oxide

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26.1 Introduction

Chromium oxide (CrO_3 , CAS-No. 1333-82-0) forms at room temperature dark red crystals (Halstenberg et al. (2000)). Chromium oxide dissolves in water and forms there chromic acid. Further liquids where this chromium compound can be dissolved are sulphuric acid and nitric acid. For this inventory the functional unit is 1 kg solid chromium oxide flakes. Its molecular weight is 99.99 g/mol. Synonyms for chromium oxide are chromic acid anhydride, chromium trioxide.

26.2 Reserves and Resources of material

The production of chromium oxide is made by the reaction of sodium dichromate with sulphuric acid (for more details see below). Therefore, all further discussion of resources equals to the discussion about these two educts used here.

26.3 Use of material / product

According to Halstenberg et al. (2000), electroplating is the most important field of application for this substance here. Therefore, a huge variety of different mixtures are on the market. Further uses of chromium oxide are passivating zinc, aluminium, cadmium and brass – the production of chromium dioxide as well as the wood preservation. The examined data source did not contain any information about the production capacities or the real production situation worldwide.

26.4 Systems characterization

In the production process for chromium oxide the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of chromium oxide is not considered to be high. For this inventory the functional unit is 1 kg of solid chromium oxide flakes. As process location Europe (RER) is used.

According to Halstenberg et al. (2000), industry distinguishes between the dry process and the wet process for the production of chromium oxide. Furthermore it is mentioned in the same time, that the dry process is not used much anymore – thus, in this study only the wet process is taken into consideration.

In this process, a hot saturated solution of sodium dichromate reacts with sulphuric acid. After 30 to 60 minutes, chromium oxide starts to precipitate from this solution. Filtering and removal of sodium hydrogen sulphate as well as several fusions and decanting steps lead to the final product: CrO_3 , chromium oxide flakes.

26.5 Chromium oxide, at plant (Location: RER)

26.5.1 Process

This dataset includes a rough estimation of the production process for chromium oxide. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approxi-

mated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The further examined production way for chromium oxide can be summarized within the following reaction equation:



26.5.2 Resources

Energy

There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the chromium oxide production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 26.1.

Raw materials and Chemicals

According to the above shown reaction equation - the following stoichiometric inputs are needed (yield 100%) for the production of 1 kg of chromium(VI)oxide:

- sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$: 1309.981 g (5.001 mol)
- sulphuric acid, H_2SO_4 : 980.798 g (10.001 mol)

For the production a yield of 98% for the overall reaction out of sodium dichromate is used (see chapter 72). Thus 1336.715 g sodium dichromate and 1000.814 g sulphuric acid are considered as raw materials in this inventory. A summary of the values used is given in Tab. 26.1.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the chromium oxide production.

As there is neither any information about the process water amount, here in this study, an amount of 25% of the cooling water amount is assumed – leading to an input of 6 kg water per kg chromium oxide.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg chromium oxide was included.

26.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg chromium oxide is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of chromium oxide. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input.

This assumption leads to air emissions of 2.673 g sodium dichromate and 2.002 g sulphuric acid.

Emissions to water

The remaining amount of unreacted substances was assumed to leave the production process with the waste water, leading to a pollution of the waste water with 24.061 g sodium dichromate and 18.015 g sulphuric acid.

Further it was assumed that all the waste water is treated in a internal waste water plant, but only 50% of the chromate is removed there, according to Zimmermann et al. (1996). Thus, the leaving water contains 4.225 g sodium ions, 9.918 g dichromate ions and 17.647 g sulphate. A summary of the values used in this inventory is given in Tab. 26.1.

By-products and solid wastes

Besides chromium oxide, sodium hydrogen sulphate is produced. According to Halstenberg et al. (2000), this substance is removed during the production process. It is accounted in this study as a by-product and therefore is in accordance with the methodology of the study not further shown in the dataset here. Other solid wastes occurring during the production of chromium oxide were neglected in this inventory.

Tab. 26.1 Energy demand, Resource demand and emissions for the production of chromium oxide.

[per kg chromium(IV)oxide]			Remark
INPUTS			
sodium dichromate	kg	1.337	stoichiometric calc., 98% yield
sulphuric acid	kg	1.001	stoichiometric calc., 98% yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m3	2.40E-02	estimation
Water, unspecified	m3	6.00E-03	estimation
transport by train	tkm	1.40E+00	standard distances
transport by lorry, 32t	tkm	2.34E-01	standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
sodium dichromate, to air	kg	2.67E-03	estimated as 0.2% of input
sulphuric acid, to air	kg	2.00E-03	estimated as 0.2% of input
sodium ions, to water	kg	4.23E-03	calculated from mass balance
dichromate ions, to water	kg	9.92E-03	calculated from mass balance
sulphate, to water	kg	1.76E-02	calculated from mass balance

26.6 Data quality considerations

Tab. 26.2 shows the data quality indicators for the inventory of chromium oxide production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the chromium oxide production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 26.9.

Tab. 26.2 Input / Output and uncertainty for the process “chromium oxide, at plant (RER)”

Explanation	Name	Location	Unit	chromium	UncertaintyType	StandardDeviation95%	GeneralComment
				oxide, flakes,			
				at plant			
Resource Technosphere Input from	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	Water, unspecified natural origin		m3	6.00E-03	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	sodium dichromate, at plant	RER	kg	1.34E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	sulphuric acid, liquid, at plant	RER	kg	1.00E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation
	transport, freight, rail	RER	tkm	1.40E+00	1	2.09	(4,5,na,na,na,na); standard distances
	transport, lorry 32t	RER	tkm	2.34E-01	1	2.09	(4,5,na,na,na,na); standard distances
	chromium oxide, flakes, at plant	RER	kg	1			
Output Air emission	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input
	Sulfate		kg	2.00E-03	1	2.32	(5,5,na,na,na,5); estimation
	Sodium dichromate		kg	2.67E-03	1	2.32	(5,5,na,na,na,5); estimation
	Sulfate		kg	1.76E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	Sodium, ion		kg	4.23E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	Dichromate		kg	9.92E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
Water emission							

26.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

26.8 Conclusions

The inventory for chromium oxide is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if chromium oxide is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

26.9 EcoSpold Meta Information

ReferenceFunction	Name	chromium oxide, flakes, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Chromsäureanhydrid,
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of solid chromium oxide flakes. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	1333-82-0
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from sodium dichromate and sulphuric acid according to the wet process scheme, having a process yield of 98%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 50% for Cr-compounds).
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

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27 Copper compounds

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 Review: Heiko Kunst, TU Berlin

27.1 Introduction

Copper compounds, although representing only a small fraction of the total copper production, play an important and varied role in industry and in agriculture. One of the oldest known fungicides was copper-based and the last 20 years have brought a resurgence in the use of copper-based fungicides due to a lack of tolerance by fungi to copper, but also due to its relatively low toxicity to higher plants and animals. Within this study here, two of these copper compounds are examined further in details: copper(II)carbonate hydroxide and copper(II)oxide:

- **Copper(II)carbonate hydroxide** ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, CAS-No. 12069-69-1), also called basic copper carbonate, occurs according to Richardson (2000b) in nature as the monoclinic mineral malachite. Another form that exists is the metastable blue mineral azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, CAS-No. 12070-39-2). Pure copper carbonate has not been isolated so far. Both of them are insoluble in water but dissolve quite good in e.g. ammonia or alkali metal cyanide solutions. Some properties of copper carbonate are given in the following table.
- **Copper(II)oxide** (CuO , CAS-No. 1317-38-0) occurs according to Richardson (2000a) in nature as the black minerals tenorite and paramelaconite. Produced CuO is therefore also black. This compound is insoluble in water as well as in alcohols – but is dissolved by alkali metal cyanides or by strong acid solutions. Some properties of copper oxide are given in the following table.

Tab. 27.1 Chemical and physical properties of copper(II)carbonate (malachite) and copper(II)oxide (according to Richardson (2000a) and Richardson (2000b))

Property	Copper(II) carbonate	Copper(II) oxide	Unit	Remarks
Molecular weight	221.12	79.54	g mol^{-1}	
Melting point	n.a.	1330	$^{\circ}\text{C}$	at normal pressure

27.2 Reserves and Resources of material

As already mentioned in the introduction, both substances are in fact existing minerals in the nature. Copper(II)carbonate hydroxide or malachite is found in nearly all copper deposits. Notable occurrences are Nizhne-Tagilsk, Siberia; Chessy, Fr.; Tsumeb, Namibia; and Bisbee, Ariz., U.S (Encyclopædia Britannica (2003)). Besides, copper(II)carbonate is produced chemically out of copper salt solutions.

Copper oxide or tenorite, found as gray-to-black metallic crystals, is a sublimation product on lavas. Melaconite, the massive variety, is common as earthy deposits in the oxidized zone of copper lodes. Crystals of tenorite have been identified at Mount Vesuvius and Mount Etna, Italy, and at Lostwithiel, Cornwall, Eng. Melaconite is abundant at Huerta de Arriba, Burgos, Spain, and at Bisbee, Arizona, where it was mined in the end of the 19th century as a copper ore (Encyclopædia Britannica (2003)). Besides, copper(II)oxide is also produced chemically out of copper or other copper compounds.

Quantitative information about either of the two compounds was not available.

27.3 Use of material / product

According to Richardson (2000a), copper carbonate is used as a precursor in the production of a variety of copper salts and soaps. Further uses are in the area of animal feeds, sweetening of petroleum, electroplating or hydrogenation catalyst. Copper oxides on the other side, is also used as a precursor of a variety of copper (II) salts, but most of it is used in the production of compounds for wood preservation. Further areas of use or application are feed industry (additives), glass and ceramic industry (pigment).

27.4 Systems characterization

27.4.1 Copper(II)carbonate

According to Richardson (2000a), two different grades of Copper(II)carbonate exist – a light and a dense one. The light one is produced usually by precipitating out of a copper(II)sulphate solution where sodium carbonate is added. For the dense form, the copper(II)salt solution is added to a sodium hydrogen carbonate solution. In both cases, after 1 to 2 hours, the reaction is completed.

Due to very few information, in this study, only the production of precipitated copper(II)carbonate with the aid of sodium carbonate is examined. Therefore an overall yield of 98% is assumed. For this inventory the functional unit is 1 kg of precipitated copper(II)carbonate. As process location Europe (RER) is used.

27.4.2 Copper(II)oxide

Most common, according to Richardson (2000a), is the use of hydrometallurgy. Therefore, a solution of ammonia and ammonium carbonate leaches metallic copper very well in the presence of air. The different steps of the process chain for the copper(II)oxide production are shown here. The yield of such a system is assumed to be 98%.

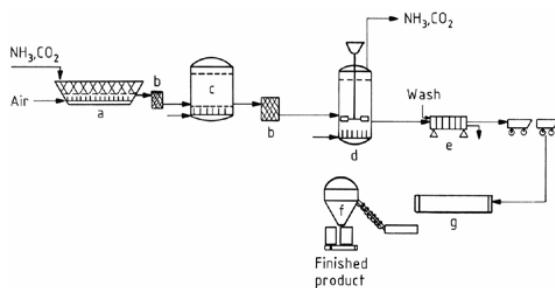


Fig. 27.1 Process chain for the production of copper(II)oxide by hydrometallurgy (Fig.1 out of Richardson (2000a) – showing leach vat [a], filter [b], treatment tank [c], strip tank [d], press [e], bag house [f] and drying kiln [g])

As the first reaction step is very slow compared with the following two steps, only a continuous operation of the plant achieves good results. After the leaching step, several filtering and stripping steps are succeeding before the copper(II)oxide can be dried and packed. The used ammonia and carbon dioxide are recovered in the strip tank and go back to the starting point.

27.5 Copper carbonate, at plant (Location: RER)

27.5.1 Process

This dataset includes a rough estimation of the production process for copper carbonate. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The overall reaction for the production of precipitated copper(II)carbonate out of copper(II) salt with the aid of sodium carbonate can be summarized as:



27.5.2 Resources

Energy

There was no information available on the amount of energy used for the above shown process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the copper carbonate production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 27.2.

Raw materials and Chemicals

According to the above shown reaction equations - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of copper carbonate:

- Copper(II)sulphate, CuSO_4 : 1443.560 g (9.044 mol)
- Sodium carbonate, Na_2CO_3 : 479.333 g (4.522 mol)

For the production a yield of 98% for the overall reaction is used. Therefore 1473.021 g copper(II)sulphate – shown here in this study as 586.993 g metallic copper and 904.487 g sulphuric acid due to the fact that no copper salts are included into the database – and 489.115 g sodium carbonate are considered as raw materials in this inventory. For the amount of process water in this study here not the stoichiometric value but a value of 0.25% compared to the cooling water amount is used. A summary of the values used is given in Tab. 27.2.

Cooling water

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the copper carbonate production.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg copper carbonate was included.

27.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg copper carbonate is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of copper carbonate. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the sulphate input of the copper salt. This assumption leads to air emissions of 0.181 g sulphate.

Emissions to water

The remaining amount of non-reacted sodium carbonate and copper sulphate are assumed to leave the production process with the waste water, leading to a pollution of the waste water with 8.804 g sodium carbonate and 29.460 g copper(II)sulphate. Further it was assumed that all the waste water is treated in an internal waste water plant. The removal efficiency for copper sulphate was assumed with 75% (based on Zimmermann et al. (1996)) leading to emissions of 2.935 g copper ions per kg product in the treated water. Sodium carbonate is dissolved in the water. All sodium and sulphate ions from the reaction are supposed to leave in the waste water – resulting in 209.94 g Na-ions and 872.74 g sulphate ions. The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of the different ingredients in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 27.2.

Solid wastes

Solid wastes occurring during the production of copper carbonate were neglected in this inventory.

Tab. 27.2 Energy demand, Resource demand and emissions for the production of copper carbonate.

[per kg copper(II)carbonate]			Remark
INPUTS			
metallic copper	kg	0.587	representing copper salt
sulphuric acid	kg	0.904	representing copper salt
sodium carbonate	kg	4.89E-01	stoichiometric calc., 98% yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m3	2.40E-02	estimation
Water, process, unspecified	m3	6.00E-03	estimation
transport by train	tkm	1.19E+00	calculated with standard distances
transport by lorry	tkm	1.98E-01	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
sulphate, to air	kg	1.81E-03	estimated as 0.2% of input
copper(II) ions, to water	kg	2.94E-03	calculated from mass balance
sulphate ions, to water	kg	8.73E-01	calculated from mass balance
sodium ions, to water	kg	2.10E-01	calculated from mass balance
COD, BOD	kg	0	calculated from water emissions
TOC, DOC	kg	1.76E-03	calculated from water emissions

27.5.4 Data quality considerations

Tab. 27.3 shows the data quality indicators for the inventory of copper carbonate production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the copper carbonate production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 27.9.

Tab. 27.3 Input / Output and uncertainty for the process “copper carbonate, at plant (RER)”

Explanation	Name	Location	Unit	copper carbonate, at plant		uncertaintyType standardDeviation95%	GeneralComment		
				RER					
				0	kg				
Resource Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	Water, unspecified natural origin		m3	6.00E-03	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	sulphuric acid, liquid, at plant	RER	kg	9.04E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	soda, powder, at plant	RER	kg	4.89E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	copper, at regional storage	RER	kg	5.87E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation		
	transport, freight, rail	RER	tkm	1.19E+00	1	2.09	(4,5,na,na,na,na); standard distances		
	transport, lorry 32t	RER	tkm	1.98E-01	1	2.09	(4,5,na,na,na,na); standard distances		
Output Air emission Water emission	copper carbonate, at plant	RER	kg	1					
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input		
	Sulfate		kg	1.81E-03	1	2.32	(5,5,na,na,na,5); estimation		
	DOC, Dissolved Organic Carbon		kg	1.76E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	TOC, Total Organic Carbon		kg	1.76E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Sulfate		kg	8.73E-01	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Sodium, ion		kg	2.10E-01	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Copper, ion		kg	2.94E-03	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		

27.6 Copper oxide, at plant (Location: RER)

27.6.1 Process

This dataset includes a rough estimation of the production process for copper(II)oxide. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The overall reaction of the three steps for the hydrometallurgical production of copper(II)oxide can be summarized out of the following two reaction steps (leaching and stripping):



27.6.2 Resources

Energy

There was no further information available on the amount of energy used in the different steps. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the copper carbonate production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 27.4.

Raw materials and Chemicals

According to the above shown reaction equations - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of copper oxide:

- copper, Cu: 798.24 g (12.571 mol)
- ammonium, NH₃: 213.702 g (12.571 mol)
- oxygen, O₂: 201.131 g (6.286 mol)
- ammonium carbonate, (NH₄)₂CO₃: 603.394 g (6.286 mol)

For the production a yield of 98% for the overall reaction out of copper is used. For ammonium and ammonium carbonate, as these substances are recovered and go back to the process, only an amount equal to the emissions to air is reported as input in this study here. Therefore 814.531 g copper, 0.427 g ammonium and 1.207 g ammonium carbonate are considered as raw materials in this inventory. Oxygen is used in the form of air and therefore not further taken into account within this inventory. A summary of the values used is given in Tab. 27.4.

Cooling water

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value is used in this inventory as approximation for the cooling water consumption of the copper(II)-oxide production.

Concerning the process water, no information is given in the examined sources. Therefore, as a first approximation, 25% of the cooling water amount are assumed for the process water, i.e. 6 kg per kg of product.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg copper carbonate was included.

27.6.3 Emissions

By-products

According to Richardson (2000a) are the produced ammonium as well as the produced carbon dioxide recovered and goes back to the start of the process – therefore, these two products are not further taken into account within this process here.

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg copper oxide is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of copper oxide. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the stoichiometric amount (without copper).

This assumption leads to air emissions of 0.427 g ammonium and 1.207 g ammonium carbonates.

Emissions to water

The remaining amount of ammonia compounds is assumed to be recovered together with the produced amounts of ammonium and carbon dioxide. As these amounts are reused, for this study here, no water emissions occurs from the copper(II)oxide production.

Solid wastes

Solid wastes occurring during the production of copper(II)oxide were neglected in this inventory.

Tab. 27.4 Energy demand, Resource demand and emissions for the production of copper(II)oxide.

[per kg copper(II)oxide]			Remark
INPUTS			
copper	kg	0.815	stoichiometric calc., 98% yield
ammonium	kg	4.27E-04	equal to emitted amount
ammonium carbonate	kg	1.21E-03	equal to emitted amount
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m ³	2.40E-02	estimation
Water, process, unspecified	m ³	6.00E-03	estimation
transport by train	tkm	4.90E-01	calculated with standard distances
transport by lorry	tkm	8.16E-02	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
ammonium, to air	kg	4.27E-04	estimated as 0.2% of stoich. amount
ammonium carbonate, to air	kg	1.21E-03	estimated as 0.2% of stoich. amount

27.6.4 Data quality considerations

The following table shows the data quality indicators for the inventory of copper(II)oxide production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the copper carbonate production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Espe-

cially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoicheometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 27.9.

Tab. 27.5 Input / Output and uncertainty for the process “copper oxide, at plant (RER)”

Explanation	Name	Location	Unit	copper oxide, at plant		uncertaintyType standardDeviation95%	GeneralComment		
				RER 0 kg					
				Infrastructure	Process				
Resource Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	Water, unspecified natural origin		m3	6.00E-03	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	ammonia, liquid, at regional storehouse	RER	kg	4.27E-04	1	1.21	(4,na,na,na,na,na); estimation - equal to emitted amount		
	copper, at regional storage	RER	kg	8.15E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	ammonium carbonate, at plant	RER	kg	1.21E-03	1	1.21	(4,na,na,na,na,na); estimation - equal to emitted amount		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation		
	transport, freight, rail	RER	tkm	4.90E-01	1	2.09	(4,5,na,na,na,na); standard distances		
	transport, lorry 32t	RER	tkm	8.16E-02	1	2.09	(4,5,na,na,na,na); standard distances		
Output Air emission	copper oxide, at plant	RER	kg	1					
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input		
	Ammonia		kg	4.27E-04	1	2.32	(5,5,na,na,na,5); estimation		
	Ammonium carbonate		kg	1.21E-03	1	2.32	(5,5,na,na,na,5); estimation		

27.7 Cumulative results and interpretation

Results of the cumulative inventory for both substances can be downloaded from the database.

27.8 Conclusions

The inventory for both copper compounds is based on the a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if one of these copper compounds is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of these materials with other, alternative products.

27.9 EcoSpold Meta Information

ReferenceFunction	Name	copper carbonate, at plant	copper oxide, at plant
Geography	Location	RER	RER
ReferenceFunction	InfrastructureProcess	0	0
ReferenceFunction	Unit	kg	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1	1
ReferenceFunction	LocalName	Kupfercarbonat, ab	Kupferoxid, ab Werk
ReferenceFunction	Synonyms		
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of solid copper(II)carbonate. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.	The functional unit represent 1 kg of solid copper(II)oxide. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	12069-69-1	1317-38-0
TimePeriod	StartDate	2000	2000
TimePeriod	EndDate	2000	2000
TimePeriod	DataValidForEntirePeriod	1	1
TimePeriod	OtherPeriodText	date of published literature	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production out of copper sulphate and sodium carbonate with an overall process yield is of 98%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt. % of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).	Production from copper(II)oxide by hydrometallurgy. Metallic copper is leached by a solution of ammonia and ammonium carbonate. The overall process yield is of 98%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt. % of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent		
Representativeness	ProductionVolume		
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	copper sulphate is included into the dataset as metallic copper and sulphuric acid due to the lack of an appropriate dataset for copper salt	
Representativeness	UncertaintyAdjustments		

27.10 References

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28 Cyclohexanol

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28.1 Introduction

Cyclohexanol ($C_6H_{11}OH$, CAS-No. 108-93-0) is at room temperature a colourless, substance that forms hygroscopic crystalline needles with a camphor-like odour (Musser (2000)). Cyclohexanol is very soluble in alcohols, ketones, ethers as well as aliphatic or aromatic hydrocarbons. For this inventory the functional unit is 1 kg solid cyclohexanol. The most important chemical and physical properties of cyclohexanol used in this inventory are given here.

Synonyms for cyclohexanol: -

Tab. 28.1 Chemical and physical properties of cyclohexanol (according to Musser (2000))

Property	Unit	Value	Remarks
Molecular weight	100.16	$g\ mol^{-1}$	
Boiling point	161.1	°C	at normal pressure
Melting point	25.15	°C	at normal pressure

28.2 Reserves and Resources of material

The production of cyclohexanol is made by hydrogenation or oxidation of either phenol, benzene or of cyclohexane (for more details see chapter 28.4) – all of them being hydrocarbons out of oil and/or gas. Therefore, all further discussion of resources equals to the discussion about the oil / gas reserves (see Dones et al. (2007)).

28.3 Use of material / product

According to Musser (2000), the two most important uses of cyclohexanol are its function as an intermediate in the production of adipic acid resp. cyclohexanone, a precursor of caprolactam. Adipic acid and caprolactam are themselves precursors for the production of nylon 6 resp. nylon 66. Besides this, cyclohexanol is also used e.g. as a solvent for lacquers, as homogenizer or stabilizer in laundries, for paint or varnish removers and in many other industries.

In 1992, the worldwide production capacity of cyclohexanol and cyclohexanone production was in the order of 3.2 Mt. Thereof, 58% was used for the caprolactam and 40% for the adipic acid production – only the remaining rest is used for further uses (Musser (2000)).

28.4 Systems characterization

In the production process for cyclohexanol the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of cyclohexanol is not considered to be high. For this inventory the functional unit is 1 kg of solid cyclohexanol. As process location Europe (RER) is used.

According to Musser (2000), three principal possibilities for the production of cyclohexanol can be, and are used industrially:

- Hydrogenation of phenol
- Oxidation of cyclohexane
- Partial hydrogenation of benzene

Nowadays, most of the production sites use a type of cyclohexane oxidation technology – the other two technologies are used only by very few companies. Due to a lack of data for cyclohexane, nevertheless, for this study here a mix of 50:50 of the two mentioned hydrogenation techniques is used. Process flow schemes for these two production routes of cyclohexanol are explained in the following paragraphs and shown in Fig. 28.1 rsp. Fig. 28.2.

According to Musser (2000), in the first case (hydrogenation of phenol), depending on the chosen catalyst, either only cyclohexanol, a mixture of it with cyclohexanone or only the latter one is produced. For this study here, the first case – a production of cyclohexanol only, is assumed. Therefore, a supported nickel catalyst or a nickel catalyst containing copper, cobalt or manganese is used. For a high yield, a vapor or a liquid –phase hydrogenation technique is used. The yield of the system is up to 98%.

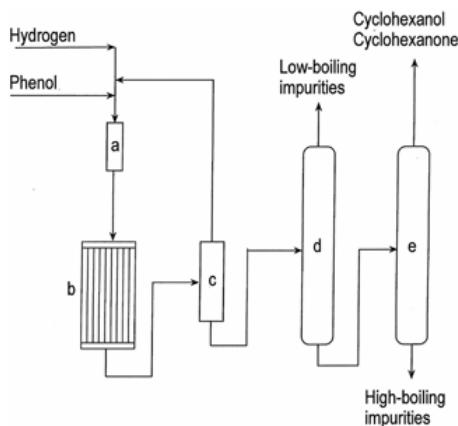


Fig. 28.1 Process chain for the production of cyclohexanol by hydrogenation of phenol (Fig.1 out of Musser (2000) – showing phenol evaporator [a], hydrogenation reactor [b], condenser [c], low-boiler removal column [d], cyclohexanol recovery column [e])

In the second case – the hydrogenation of benzene – three steps can be distinguished: (i) a selective hydrogenation of benzene, (ii) a separation from the produced cyclohexene from unreacted benzene rsp. over-reacted cyclohexane and (iii) the hydration of cyclohexene to cyclohexanol. In both reaction steps, catalysts are used. The first reaction is thereby run only until a conversion of about 50% of the benzene input into cyclohexene (35%) and cyclohexane (15%) – the remaining benzene is then recovered, while cyclohexane is either sold or re-synthesized into benzene. The overall yield of the production of cyclohexanol for this case here is in the order of 95%.

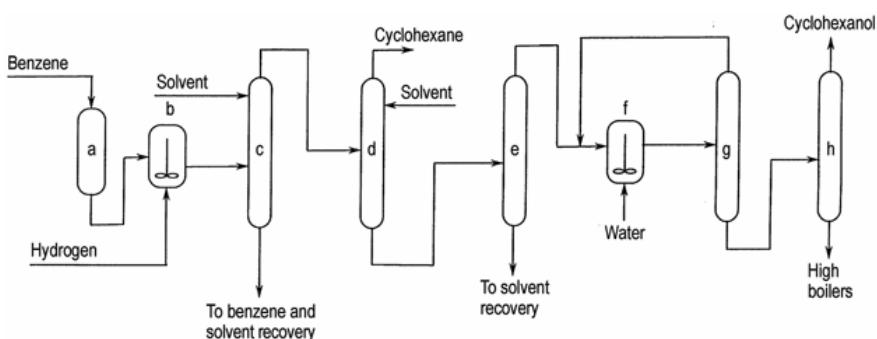


Fig. 28.2 Process chain for the production of cyclohexanol by partial hydrogenation of benzene (Fig.4 out of Musser (2000) – showing benzene purification [a], partial hydrogenation [b], separation excess benzene [c], isolation of cyclohexene [d] & [e], hydration of cyclohexene [f], cleaning/isolation of cyclohexanol [g] & [h])

28.5 Cyclohexanol, at plant (Location: RER)

28.5.1 Process

This dataset includes a rough estimation of the production process for cyclohexanol. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The two examined production ways for cyclohexanol can be summarized within the following reaction equations:



28.5.2 Resources

Energy

There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the cyclohexanol production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 28.2.

Raw materials and Chemicals

According to the above shown reaction equations - the following stoichiometric inputs are needed (yield 100%) for the production of 0.5 kg of cyclohexanol by either of the two ways:

- phenol, C₆H₅: 469.25 g (4.992 mol)
- benzene, C₆H₆: 389.93 g (4.992 mol)
- hydrogen, H₂: 29.95 g (4.992 mol)

For the production a yield of 98% for the hydrogenation of phenol and 95% for the overall reaction out of benzene is used. For benzene, as the un-reacted part is recovered and goes back to the process again, an amount equal to the stoichiometric amount plus the emissions to air is reported as input in this study here.

Therefore 478.826 g phenol, 393.824 g benzene and 51.582 g hydrogen are considered as raw materials in this inventory. A summary of the values used is given in Tab. 28.2.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the cyclohexanol production.

For the process water amount, a stoichiometric amount of 89.86 g can be calculated in the case of the reaction out of benzene. For the other production route, no data about water consumption are given. For this study here, an amount of 25% of the cooling water amount is assumed – leading to an input of 6 kg water per kg cyclohexanol.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg cyclohexanol was included.

28.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg cyclohexanol is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of cyclohexanol. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input – for benzene, an emission of 1% was assumed.

This assumption leads to air emissions of 0.958 g phenol, 3.899 g benzene and 1.030 g hydrogen.

Emissions to water

In the first reaction, the remaining amount of unreacted phenol was assumed to leave the production process with the waste water, leading to a pollution of the waste water with 8.62 g phenol. Further it was assumed that all the waste water is treated in an internal waste water plant. The removal efficiency for phenol was assumed with 90% leading to emissions of 0.862 g phenol per kg product in the treated water. The carbon contained in the removed phenol was accounted as CO₂ emissions to air (21.79 g CO₂ per kg product). The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of phenol in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 28.2.

In case of the second reaction, water is only used in the second part of the process (hydration of cyclohexene). There is no information about possible waste water emissions in this process. Therefore, for this study the values of CO₂ to air as well as COD, BOD, TOC and DOC from the phenol process are used for the whole reaction.

Solid wastes

Solid wastes occurring during the production of cyclohexanol were neglected in this inventory.

Tab. 28.2 Energy demand, Resource demand and emissions for the production of cyclohexanol.

[per kg cyclohexanol]			Remark
INPUTS			
phenol	kg	0.479	stoichiometric calc., 98% yield
benzene	kg	0.394	stoichiometric calc., 100% excess
hydrogen	kg	0.052	stoichiometric calc., 96% total yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m ³	2.40E-02	estimation
Water, unspecified	m ³	6.00E-03	estimation
transport by train	tkm	5.55E-01	standard distances
transport by lorry, 32t	tkm	9.24E-02	standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
phenol, to air	kg	9.58E-04	estimated as 0.2% of input
benzene, to air	kg	3.90E-03	estimated as 0.2% of input
hydrogen, to air	kg	1.03E-03	estimated as 0.2% of input
carbon dioxide, fossil, to air	kg	4.36E-02	from waste water treatment
phenol, to water	kg	8.62E-04	calculated from mass balance
COD, BOD	kg	1.97E-03	calculated from water emissions
TOC, DOC	kg	6.60E-04	calculated from water emissions

28.6 Data quality considerations

The following table shows the data quality indicators for the inventory of cyclohexanol production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the cyclohexanol production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical

process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 28.9.

Tab. 28.3 Input / Output and uncertainty for the process “cyclohexanol, at plant (RER)”

Explanation	Name	Location	Unit	cyclohexanol, at plant	uncertaintyType	StandardDeviation95%	GeneralComment	
							Location	RER
							InfrastructureProcess	0 kg
Resource	Water, cooling, unspecified natural origin	m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	Water, unspecified natural origin	m3	6.00E-03	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	phenol, at plant	RER	kg	4.79E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	benzene, at plant	RER	kg	3.94E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	hydrogen, liquid, at plant	RER	kg	5.20E-02	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation	
	transport, freight, rail	RER	tkm	5.55E-01	1	2.09	(4,5,na,na,na,na); standard distances	
	transport, lorry 32t	RER	tkm	9.24E-02	1	2.09	(4,5,na,na,na,na); standard distances	
Input from Technosphere	cyclohexanol, at plant	RER	kg	1				
	Heat, waste	MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input		
	Carbon dioxide, fossil	kg	4.36E-02	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Hydrogen	kg	1.03E-03	1	2.32	(5,5,na,na,na,5); estimation		
	Benzene	kg	3.90E-03	1	2.32	(5,5,na,na,na,5); estimation		
	Phenol	kg	9.58E-04	1	2.32	(5,5,na,na,na,5); estimation		
	BOD5, Biological Oxygen Demand	kg	1.97E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	COD, Chemical Oxygen Demand	kg	1.97E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	DOC, Dissolved Organic Carbon	kg	6.60E-04	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	TOC, Total Organic Carbon	kg	6.60E-04	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
Output Air emission	Phenol	kg	8.62E-04	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		

28.7 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

28.8 Conclusions

The inventory for cyclohexanol is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if cyclohexanol is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

28.9 EcoSpold Meta Information

ReferenceFunction	Name	cyclohexanol, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Cyclohexanol, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of solid cyclohexanol. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	108-93-0
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production is a 50:50 mix from hydrogenation of phenol and partial hydrogenation of benzene with a process yield of 98% (phenol) resp. 95% (benzene). Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

28.10 References

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29 Dimethyl ether

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29.1 Introduction

Dimethyl ether (C_2H_6O , CAS-No. 115-10-6) is the simplest form of aliphatic ethers having the following structure: $H_3C—O—CH_3$. According to Müller & Hübsch (2000) it is a colourless and almost odourless gas at room temperature. The most important chemical and physical properties of dimethyl ether are given here.

Tab. 29.1 Chemical and physical properties of dimethyl ether (data from Müller & Hübsch (2000))

Property	Value	Dimethyl ether	Remarks
Molecular weight	$g\ mol^{-1}$	46.07	
Density	$kg\ m^{-3}$	668.3	at 20 °C
Boiling point	°C	- 24.8	at normal pressure
Melting point	°C	- 141	at normal pressure

29.2 Reserves and Resources of material

For a long time, dimethyl ether was a by-product of the high pressure methanol production process. Due to the fact, that this type of methanol production sites is almost everywhere closed down, special plants for the production of dimethyl ether have been build up. According to Müller & Hübsch (2000) is the Western European production of dimethyl ether about 50 kt per year - with production plants in Germany, Switzerland and the Netherlands.

29.3 Use of material / product

Dimethyl ether is mainly used as educt for the production of dimethyl sulphate. A further use is the use as an aerosol propellant.

29.4 Systems characterization

In the production process for dimethyl ether the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of dimethyl ether is not considered to be high.

According to Müller & Hübsch (2000) dimethyl ether is produced from methanol in the presence of an acidic catalyst - i.e. zinc chloride, iron chloride, copper sulphate and many more. The most important catalysts used in industrial production are aluminium oxide and aluminium silicate. The functional unit for the inventory is 1 kg of dimethyl ether. As process location Europe (RER) is used.

29.5 Dimethyl ether, at plant (Location: RER)

29.5.1 Process

This dataset includes a rough estimation of the production process of dimethyl ether from methanol. The used catalyst is not taken into account. Due to missing production data this inventory bases on information given in Müller & Hübsch (2000). The emissions to air and water were estimated using mass balance. It was assumed that wastewater is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is quite large. The overall reaction for the production of dimethyl ether can be formulated as follows:



A typical flow scheme for the industrial production of dimethyl ether is shown here.

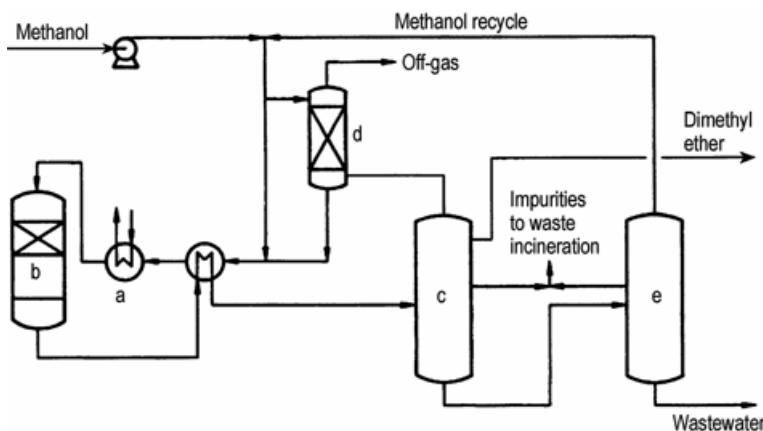


Fig. 29.1 flow scheme for the production of dimethyl ether by dehydration of methanol, with a) vaporizer, b) reactor, c) dimethyl ether column, d) scrubber, e) methanol column (Fig. 1 from Müller & Hübsch (2000))

According to Müller & Hübsch (2000) this reaction is carried out in a pipe reactor. The product is cooled in two stages as well as distilled - resulting in pure dimethyl ether. Unreacted methanol is separated from water in a second column and recycled.

29.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the wastewater treatment. Fossil fuel is needed to generate the desired heat within the process scheme. There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the dimethyl ether production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was used. A summary of the values used is given in Tab. 29.2.

Raw materials and Chemicals

For the production of dimethyl ether out of methanol the following stoichiometric inputs are needed (yield each time 100%):

- Methanol, CH₃OH: 1390.92 g (43.41 mol)

For the input of methanol, a yield of 95% is used in this study. To produce 1 kg dimethyl ether therefore 1.464 kg methanol are used.

Water use

There was no information available on the amount of cooling water used within the plant, although there has to be a respective use. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the ethanolamines production. According to the ongoing IPPC activities of the European Commission, the cooling water demand may reach 86 kg kWh⁻¹ for an once through cooling system, which would lead to a cooling water demand of 48 kg per kg product for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m³ cooling water per kg product was used.

As there is also no information about the process water consumption, a process water amount of 25% compared to the cooling water amount is assumed for this study.

Transport

Standard distances and means according to Frischknecht et al. (2007) are used for all input materials due to the fact that no information is available in Müller & Hübsch (2000).

29.5.3 Emissions

Waste heat

It was assumed that 100% of the electricity consumed is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of dimethyl ether. As approximation the air emissions occurring from the purge vent, the distillation vent and fugitive emission sources were estimated to 0.2% of the raw material input.

This assumption leads to air emissions of 2.93 g of methanol per kg produced dimethyl ether.

Emissions to water

From remaining amount of unreacted raw materials 90% are assumed to be recovered and recycled within the production plant while the remaining 10% leaves the production process with the wastewater. This assumption leads to a pollution of the wastewater with 7.03 g methanol per kg product. Further it was assumed that this wastewater is treated in an internal wastewater plant. Therefore, a removal

efficiency of 90% for methanol was assumed, leading to 0.70 g methanol in the treated water. The carbon contained in the removed methanol was accounted as CO₂ emissions to air (8.69 g CO₂ per kg product). The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of propene in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used.

A summary of the values used in this inventory is given in Tab. 29.2.

Solid wastes

Solid wastes occurring during the production of dimethyl ether were neglected in this inventory.

Tab. 29.2 Energy demand, resource demand and emissions for the production of dimethyl ether

[per kg dimethyl ether]			Remark
INPUTS			
methanol	kg	1.46E+00	stoechiometric calc., 95% yield
Water, unspecified	m ³	6.00E-03	estimation - based on cooling water input
Electricity, medium voltage	kWh	3.33E-01	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m ³	2.40E-02	estimation
Transport, by train	tkm	8.78E-01	standard distances & means
Transport, by lorry	tkm	1.46E-01	standard distances & means
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
methanol, to air	kg	2.93E-03	estimated as 0.2% of input
carbon dioxide, fossil, to air	kg	8.69E-03	from waste water treatment
methanol, to water	kg	7.00E-04	calculated from mass balance
COD, BOD	kg	1.01E-02	calculated from water emissions
TOC, DOC	kg	2.64E-03	calculated from water emissions

29.5.4 Infrastructure

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg dimethyl ether was included.

29.6 Data quality considerations

The following table shows the data quality indicators for the inventory of the dimethyl ether production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the dimethyl ether production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoechiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used

for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data.

Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 29.9.

Tab. 29.3 Input / Output and uncertainty values for the process “dimethyl ether, at plant (RER)”

Explanation	Name	Location	Unit	dimethyl ether, at plant		standardDeviation95%	GeneralComment
				RER	0 kg		
				uncertaintyType			
Resource Input from Technosphere	Water, cooling, unspecified natural origin	GLO	m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	Water, unspecified natural origin		m3	6.00E-03	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	methanol, at plant		kg	1.46E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	electricity, medium voltage, production UCTE, at grid		UCTE	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	heat, natural gas, at industrial furnace >100kW		RER	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	chemical plant, organics		RER	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation
	transport, freight, rail		RER	8.78E-01	1	2.09	(4,5,na,na,na,na); standard distances
Output Air emission Water emission	transport, lorry 32t		RER	1.46E-01	1	2.09	(4,5,na,na,na,na); standard distances
	dimethyl ether, at plant	RER	kg	1			
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input
	Carbon dioxide, fossil		kg	8.69E-03	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	Methanol		kg	2.93E-03	1	2.32	(5,5,na,na,na,5); estimation
	BOD5, Biological Oxygen Demand		kg	1.01E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	COD, Chemical Oxygen Demand		kg	1.01E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
Water emission	DOC, Dissolved Organic Carbon	RER	kg	2.64E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	TOC, Total Organic Carbon		kg	2.64E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	Methanol		kg	7.00E-04	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.

29.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

29.8 Conclusions

The inventory for dimethyl ether is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if dimethyl ether is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

29.9 EcoSpold Meta Information

ReferenceFunction	Name	dimethyl ether, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Dimethylether, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of gaseous dimethyl ether. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	115-10-6
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from methanol with a process yield of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	50 kt in Western Europe
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

29.10 References

- Frischknecht et al. (2007) Frischknecht R., Althaus H.-J., Doka G., Dones R., Hischier R., Hellweg S., Jungbluth N., Kellenberger D., Nemecek T., Rebitzer G. and Spielmann M. (2007) Overview and Methodology. Final report ecoinvent Data v2.0 No. 1. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.
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30 Dimethyl sulphate

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30.1 Introduction

Dimethyl sulphate ($C_2H_6O_4S$, CAS-No. 77-78-1) is one of the most important dialkyl sulphates - neutral esters of sulphuric acid and aliphatic alcohols. Dimethyl sulphate is a liquid at room temperature. It is completely miscible with polar organic solvents and aromatic hydrocarbons - its solubility in water is poor. The most important chemical and physical properties of water-free (anhydrous) dimethyl sulphate are given here.

Tab. 30.1 Chemical and physical properties of dimethyl sulphate (data from Weisenberger & Sandler (2000))

Property	Value	Dimethyl sulphate	Remarks
Molecular weight	$g\ mol^{-1}$	126.11	
Density	$g\ cm^{-3}$	1.329	at 20 °C
Boiling point	°C	188.8	at normal pressure
Melting point	°C	-31	at normal pressure

30.2 Reserves and Resources of material

According to Weisenberger & Sandler (2000) is the Western European production of dimethyl sulphate about 50 kt per year - with production plants in Germany, France, Switzerland and the United Kingdom.

30.3 Use of material / product

Dimethyl sulphate is mainly used in chemical reactions - especially in alkylation reactions. A classic use therefore is, according to Weisenberger & Sandler (2000), the use of dimethyl sulphate to etherize an aromatic hydroxyl group in an aqueous alkaline solution.

Further uses can be the use as a source of activators in thermosetting resins, as stabilizers for chemicals or as selective solvents for aromatic compounds out of petroleum fractions. Furthermore, dimethyl sulphate can act as catalyst in certain reactions.

30.4 Systems characterization

In the production process for dimethyl sulphate the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of dimethyl sulphate is not considered to be high.

According to Weisenberger & Sandler (2000), different production ways are possible, depending on the chosen raw materials: Ethers and sulphur trioxide / Olefins and sulphuric acid / Alcohols and chlorosulphuric acid / Alcohols and sulfonyl chloride (or thionyl chloride) / or Alcohols and sulphuric acid. According to the information in Weisenberger & Sandler (2000), the first one is used industrially for the production of dimethyl sulphate. For this study, only this production route is further examined. The functional unit for the inventory is 1 kg of anhydrous dimethyl sulphate. As process location Europe (RER) is used.

30.5 Dimethyl sulphate, at plant (Location: RER)

30.5.1 Process

This dataset includes a rough estimation of the production process of dimethyl sulphate from ethers and sulphur trioxide. Due to missing production data this inventory bases on information given in Weisenberger & Sandler (2000). The emissions to air and water were estimated using mass balance. It was assumed that wastewater is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is quite large.

The overall reaction for the production of dimethyl sulphate out of ethers and sulphur trioxide can be formulated as follows:



According to Weisenberger & Sandler (2000), this reaction takes place in water-cooled vertical steel tubes at a constant temperature of about 70°C. Thereby, stoichiometric quantities of the two educts are fed in and form quickly an acidic adduct that slowly rearranges to the neutral ester. The product is kept for hours at this temperature to avoid as much as possible the presence of acidic adducts. Further treatment until the ready product contains vacuum distillation to remove most of the still remaining impurities.

30.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the wastewater treatment. Fossil fuel is needed to generate the desired heat within the process scheme. There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the dimethyl sulphate production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was used. A summary of the values used is given in Tab. 30.2.

Raw materials and Chemicals

For the production of dimethyl sulphate out of esters and sulphur trioxide the following stoichiometric inputs are needed (yield each time 100%):

- Dimethyl ether, (CH₃)₂O (g): 365.32 g (7.93 mol)
- Sulphur trioxide, SO₃ (l): 634.84 g (7.93 mol)

For the input of the two raw materials, a yield of 95% is used in this study. To produce 1 kg dimethyl sulphate therefore 384.54 g dimethyl ether and 668.26 g sulphur trioxide are used.

Water use

There was no information available on the amount of cooling water used within the plant, although there has to be a respective use. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the dimethyl sulphate production. According to the ongoing IPPC activities of the European Commission, the cooling water demand may reach 86 kg kWh^{-1} for a once through cooling system, which would lead to a cooling water demand of 48 kg per kg product for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m^3 cooling water per kg product was used.

As there is also no information about the process water consumption, a process water amount of 25% compared to the cooling water amount is assumed for this study.

Transport

Standard distances and means according to Frischknecht et al. (2007) are used for all input materials due to the fact that no information is available in Weisenberger & Sandler (2000).

30.5.3 Emissions

Waste heat

It was assumed that 100% of the electricity consumed is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of dimethyl sulphate. As approximation the air emissions occurring from the purge vent, the distillation vent and fugitive emission sources were estimated to 0.2% of the raw material input.

This assumption leads to air emissions of 0.77 g of dimethyl ether (shown as “hydrocarbons, aliphatic, unspecified”) and 2.67 g of sulphur trioxide (expressed as 3.2 g sulphate) per kg produced dimethyl sulphate.

Emissions to water

The remaining amount of unreacted raw materials was assumed to leave the production process with the wastewater. This assumption leads to a pollution of the wastewater with 18.45 g dimethyl ether and 30.75 g sulphur trioxide per kg product. Further it was assumed that this wastewater is treated in an internal wastewater plant. Therefore, a removal efficiency of 90% for dimethyl ether was assumed, leading to 1.85 g dimethyl ether (shown as “hydrocarbons, aliphatic, unspecified”) in the treated water. The carbon contained in the removed dimethyl ether was accounted as CO₂ emissions to air (31.71 g CO₂ per kg product). For the sulphur trioxide within the wastewater it is assumed that this is decomposed to sulphuric acid and this one goes 100% to the treated water, i.e. that it has 36.87 g SO₄²⁻ per kg product in the treated water. The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of dimethyl ether in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used.

A summary of the values used in this inventory is given in Tab. 30.2.

Solid wastes

Solid wastes occurring during the production of dimethyl sulphate were neglected in this inventory.

Tab. 30.2 Energy demand, resource demand and emissions for the production of dimethyl sulphate

[per kg dimethyl sulphate]		Remark
INPUTS		
dimethyl ether	kg	3.86E-01
sulphur trioxide	kg	6.68E-01
Water, unspecified	m3	6.00E-03
Electricity, medium voltage	kWh	3.33E-01
Natural gas, burned in industrial furnace >100kW	MJ	2
Water, cooling, unspecified	m3	2.40E-02
Transport, by train	tkm	6.32E-01
Transport, by lorry	tkm	1.05E-01
chemical plant, organics	unit	4.00E-10
OUTPUTS		
waste heat, to air	MJ	1.20E+00
dimethyl ether, to air	kg	7.70E-04
sulphate, to air	kg	3.20E-03
carbon dioxide, fossil, to air	kg	3.17E-02
dimethyl ether, to water	kg	1.85E-03
sulphate (SO_4^{2-}), to water	kg	3.69E-02
COD, BOD	kg	4.28E-02
TOC, DOC	kg	9.62E-03

30.5.4 Infrastructure

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of 4×10^{-10} units per kg dimethyl sulphate was included.

30.6 Data quality considerations

The following table shows the data quality indicators for the inventory of the dimethyl sulphate production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the dimethyl sulphate production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data.

Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 30.9.

Tab. 30.3 Input / Output and uncertainty values for the process “dimethyl sulphate, at plant (RER)”

Explanation	Name	Location	Unit	dimethyl sulphate, at plant		UncertaintyType	StandardDeviation95%	GeneralComment
				RER	0 kg			
				Infrastructure	Process			
Resource Input from Technosphere	Water, cooling, unspecified natural origin	m3	2.40E-02	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant		
	Water, unspecified natural origin	m3	6.00E-03	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	dime th thyl ether, at plant	RER	kg	3.86E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	sulphur trioxide, at plant	RER	kg	6.68E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant	
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant	
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation	
	transport, freight, rail	RER	tkm	6.32E-01	1	2.09	(4,5,na,na,na,na); standard distances	
	transport, lorry 32t	RER	tkm	1.05E-01	1	2.09	(4,5,na,na,na,na); standard distances	
	dimethyl sulphate, at plant	RER	kg	1				
Output Air emission Water emission	Heat, waste	MJ	1.20E+00	1	1.88	(5.5,1,1,4,5); calculated from electricity input		
	Carbon dioxide, fossil	kg	3.17E-02	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Sulfate	kg	3.20E-03	1	2.32	(5,5,na,na,na,5); estimation		
	Hydrocarbons, aliphatic, unsaturated	kg	7.70E-04	1	2.32	(5,5,na,na,na,5); estimation		
	BOD5, Biological Oxygen Demand	kg	4.28E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	COD, Chemical Oxygen Demand	kg	4.28E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	DOC, Dissolved Organic Carbon	kg	9.62E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	TOC, Total Organic Carbon	kg	9.62E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Sulfate	kg	3.69E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Hydrocarbons, aliphatic, unsaturated	kg	1.85E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		

30.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

30.8 Conclusions

The inventory for dimethyl sulphate is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if dimethyl sulphate is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

30.9 EcoSpold Meta Information

ReferenceFunction	Name	dimethyl sulphate, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Dimethylsulfat, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid dimethyl sulphate. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	77-78-1
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from dimethyl ether and sulphur trioxide with a process yield of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	50 kt in Western Europe
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

30.10 References

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31 Epoxy Resins

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Last Changes:

2004

Summary

This chapter describes the energy and material flows for the production of epoxy resins and cast resin insulators over the life cycle from production to the gate of the factory. The investigation is based on environmental data provided in a European study of the chemical industry and on a literature research. Two approaches for the use of cumulative raw data are compared here for the example of epoxy resins. Energy use in the life cycle is an important reason for environmental impacts caused. If filling materials are added to the resins during manufacture, as e.g. for insulator products, the environmental impacts of the final product are lower than for the pure epoxy resins. The life cycle inventories presented in this report, can be used in life cycle assessment for complex products where epoxy resins or cast resin insulators are used as materials.

Keywords

Epoxy resin, Cast resin insulator, Aluminium oxide

31.1 Introduction

Epoxy resins are used in a wide variety of products. This inventory for epoxy resins can be used as a background database for the preparation of life cycle assessments for technical products such as equipment for electricity transmission or photovoltaic systems.

31.2 Reserves, Resources, Characterisation and Use of Product

Epoxy resins are a product of the chemical industry. Crude oil and natural gas are the main primary resources used. Epoxy resins (CAS no. 25928-94-3) are sold as a liquid. They are used in a wide variety of products, e.g. for the preparation of glass fibre reinforced plastics.

31.3 System Characterisation

Patel et al. (1999) investigated a cumulative energy demand of 107 MJ/kg for epoxy resins, but no process specific emissions. The life cycle inventory for liquid epoxy resins is based on the APME inventory (Boustead 1997; 1999). The total energy use (renewable and non-renewable sources) is reported to be 140.7 MJ/kg. This inventory shows only the aggregated figures for the whole production chain.

Fig. 31.1 shows the life cycle of liquid epoxy resins as it was modelled by Boustead (1999). The left hand side shows a general overview for the life cycle stages from raw material extraction to the production. The right hand side shows a more detailed view for the last stage of epoxy resin production.

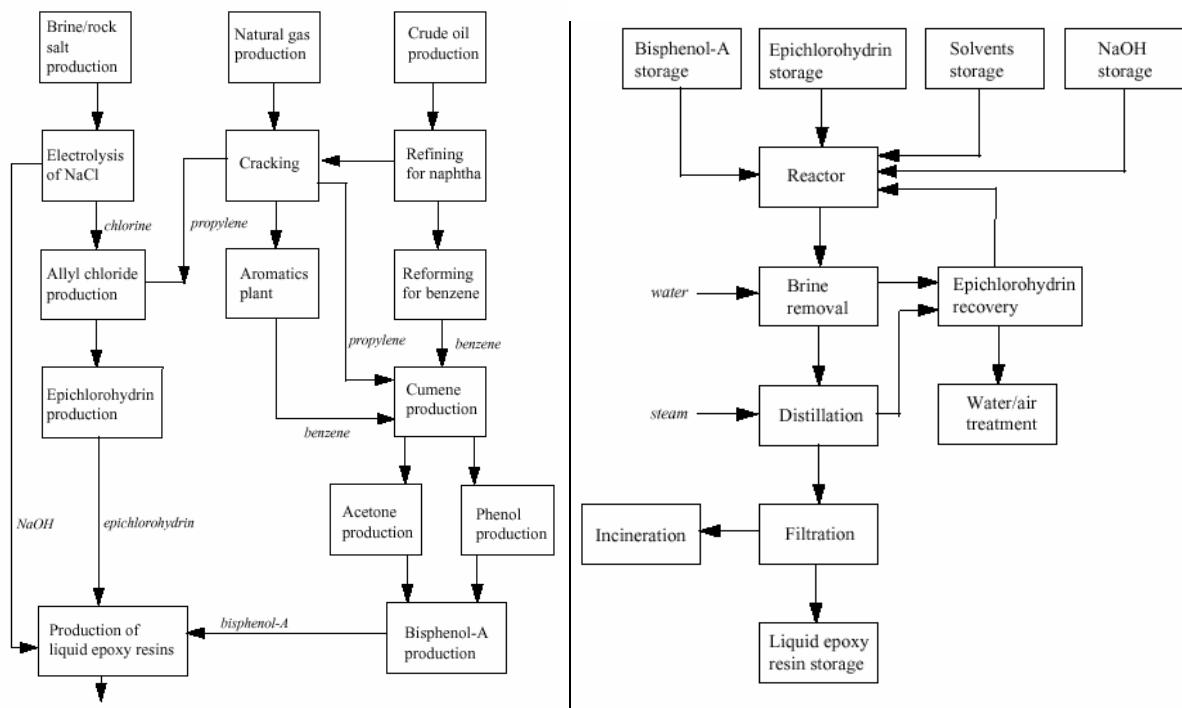


Fig. 31.1 Outline sequence of operations required to produce liquid epoxy resins from raw resources (left hand side) and detailed operations for the production of liquid epoxy resins (right hand side) (Boustead 1999).

31.4 Life Cycle Inventories

Only cumulative data of the complete product systems are published, e.g. the total amount of CO₂ emitted in the life cycle of a product or service, but no information, e.g. on the specific energy consumption or on process specific emissions in different stages is provided. The cumulative data do not cover all important aspects like land occupation and they handle certain aspects like the treatment of waste in a way that is not compatible with the ecoinvent database. The background data, e.g. for electricity supply or for transport services are different from the ones in the database and they might be outdated. However, they cannot be corrected if only cumulative data are available. Uncertainties of the respective figures are mostly unknown.

There are two principal approaches how to integrate such cumulative data in a database like ecoinvent that collects data on a unit process basis. The first one is a direct implementation of the reported cumulative flows without any linkage to other datasets in the database. The second possibility is a disaggregation of cumulative data based on the available information. For instance, the amount of crude oil extracted is used to assess the demand for fuel oil in combustion processes, or the reported amount of water resource use is assumed to be a demand for tap water, etc.

The first approach leaves the whole responsibility for the data quality to the original data generator, as data are not changed. New developments like for instance a more efficient electricity supply cannot be considered. Aspects which are not considered in the original data are completely neglected (e.g. land use). Models applied for transport distances or waste management options differ from the standards set for the database.

The second approach makes the data more comparable to the other unit processes in the database. E.g. all emissions of combustion processes are taken into account with the same assumptions. But there are large uncertainties due to the assumptions required while disaggregating the data.

In this chapter we used both approaches for the example of epoxy resin production. The standard procedure in the ecoinvent project is the direct use of cumulative data without a disaggregation.

31.4.1 Epoxy resin, cumulative data

The inventory has been elaborated by Boustead (1999). It is used here in the original form according to the approach described in the chapter about the integration of APME data into the database ecoinvent. Figures given as e.g. “<1” are interpreted as 0.5. Only the disposal option for the amount of reported wastes have been modelled with background data from the database. Tab. 31.1 shows the life cycle inventory based cumulative data for the life cycle.

For all other processes in the ecoinvent database data quality is assessed with information about the standard deviation, a probability function (always lognormal) and a clarifying comment. Due to the lack of respective information in the original source (Boustead 1997; 1999), no uncertainty assessment was possible. The data quality is poor because it is not possible to link these data to the background data of the ecoinvent database.

For the calculation of a resin use within an LCI it would be necessary to include also the use of curing agents or hardeners that are used in order to produce hardened epoxy resins for the final use. Due to the variety of possible curing agents it is extremely difficult to get the necessary LCI data for these chemicals. Boustead (1997:4) assumes that the use of data for liquid epoxy resins will provide in many cases a reasonable approximation for an epoxy system.

Tab. 31.1 Life cycle inventory for the production of liquid epoxy resin based on cumulative data for the life cycle (Boustead 1999).

(next side)

31. Epoxy Resins

	Name	Locati on	Infrast uct	Unit	epoxy resin, liquid, at plant	Under stand	GeneralComment
	Location	Infrastructure	Process	Unit	RER 0 kg		
product	epoxy resin, liquid, at plant	RER	0	kg	1.00E+0		
solid waste	disposal, hard coal mining waste tailings, in surface backfill	GLO	0	kg	3.00E-1	Uncertainty for LCI results cannot be determined, Table 8, update 1999	
	disposal, municipal solid waste, 22.9% water, to sanitary landfill	CH	0	kg	4.51E-2	Uncertainty for LCI results cannot be determined, Table 8, update 2000	
	disposal, average incineration residue, 0% water, to residual material landfill	CH	0	kg	6.10E-2	Uncertainty for LCI results cannot be determined, Table 8, update 2001	
	disposal, hazardous waste, 0% water, to underground deposit	DE	0	kg	1.90E-2	Uncertainty for LCI results cannot be determined, Table 8, update 2002	
	disposal, facilities, chemical production	RER	0	kg	3.20E-5	Uncertainty for LCI results cannot be determined, Table 8, update 2003	
	disposal, municipal solid waste, 22.9% water, to municipal incineration	CH	0	kg	5.80E-3	Uncertainty for LCI results cannot be determined, Table 8, update 2004	
	disposal, plastics, mixture, 15.3% water, to sanitary landfill	CH	0	kg	4.30E-4	Uncertainty for LCI results cannot be determined, Table 8, update 2005	
	disposal, wood untreated, 20% water, to municipal incineration	CH	0	kg	2.00E-5	Uncertainty for LCI results cannot be determined, Table 8, update 2006	
energy resources	Oil, crude, in ground	-	-	kg	6.70E-1	Uncertainty for LCI results cannot be determined, Table 3, update 1999	
	Gas, natural, in ground	-	-	Nm3	2.13E+0	Uncertainty for LCI results cannot be determined, Table 3, update 1999	
	Coal, hard, unspecified, in ground	-	-	kg	3.60E-1	Uncertainty for LCI results cannot be determined, Table 3, update 1999	
	Coal, brown, in ground	-	-	kg	2.10E-1	Uncertainty for LCI results cannot be determined, Table 3, update 1999	
	Peat, in ground	-	-	kg	8.30E-4	Uncertainty for LCI results cannot be determined, Table 3, update 1999	
	Wood, unspecified, standing	-	-	m3	3.04E-6	Uncertainty for LCI results cannot be determined, Table 3, update 1999	
	Energy, gross calorific value, in biomass	-	-	MJ	2.06E-1	Uncertainty for LCI results cannot be determined, Table 3, update 1999	
	Energy, potential, stock, in barrage water	-	-	MJ	1.30E+0	Uncertainty for LCI results cannot be determined, Table 3, update 1999	
	Uranium, in ground	-	-	kg	2.22E-5	Uncertainty for LCI results cannot be determined, Table 3, update 1999	
material resources	Barite, 15% in crude ore, in ground	-	-	kg	4.10E-4	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Aluminium, 24% in bauxite, 11% in crude ore, in ground	-	-	kg	1.27E-3	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Clay, bentonite, in ground	-	-	kg	1.30E-4	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Anhydrite, in ground	-	-	kg	1.30E-5	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Chromium, 25.5 in chromite, 11.6% in crude ore, in ground	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Clay, unspecified, in ground	-	-	kg	1.40E-5	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Dolomite, in ground	-	-	kg	2.90E-4	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Feldspar, in ground	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Manganese, 35.7% in sedimentary deposit, 14.2% in crude ore, in ground	-	-	kg	2.84E-6	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Fluorspar, 92%, in ground	-	-	kg	3.90E-5	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Granite, in ground	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Gravel, in ground	-	-	kg	8.00E-6	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Iron, 46% in ore, 25% in crude ore, in ground	-	-	kg	2.40E-3	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Lead, 5%, in sulfide, Pb 2.97% and Zn 5.34% in crude ore, in ground	-	-	kg	4.00E-6	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Calcite, in ground	-	-	kg	7.10E-1	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Nickel, 1.13% in sulfide, Ni 0.76% and Cu 0.76% in crude ore, in ground	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Olivine, in ground	-	-	kg	2.10E-5	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Phosphorus, 18% in apatite, 12% in crude ore, in ground	-	-	kg	2.20E-4	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Sylvite, 25 % in sylvinitic, in ground	-	-	kg	2.90E-2	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Rutile, in ground	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Sand, unspecified, in ground	-	-	kg	1.20E-3	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Shale, in ground	-	-	kg	3.70E-5	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Sodium chloride, in ground	-	-	kg	1.80E+0	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Sulfur, in ground	-	-	kg	7.30E-3	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
	Zinc 9%, in sulfide, Zn 5.34% and Pb 2.97% in crude ore, in ground	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 4, update 1999	
water	Water, unspecified natural origin	-	-	m3	1.91E-2	Uncertainty for LCI results cannot be determined, Table 5, update 1999	
	Water, river	-	-	m3	9.20E-5	Uncertainty for LCI results cannot be determined, Table 5, update 1999	
	Water, salt, ocean	-	-	m3	9.50E-5	Uncertainty for LCI results cannot be determined, Table 5, update 1999	
	Water, well, in ground	-	-	m3	1.40E-5	Uncertainty for LCI results cannot be determined, Table 5, update 1999	
	Water, cooling, unspecified natural origin	-	-	m3	3.84E-1	Uncertainty for LCI results cannot be determined, Table 5, update 1999	
emissions to air	Particulates, > 10 um	-	-	kg	4.80E-3	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Particulates, > 2.5 um, and < 10um	-	-	kg	6.45E-3	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Particulates, < 2.5 um	-	-	kg	3.75E-3	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Carbon monoxide, fossil	-	-	kg	2.20E-3	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Carbon dioxide, fossil	-	-	kg	5.90E+0	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Sulfur dioxide	-	-	kg	1.90E-2	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Nitrogen oxides	-	-	kg	3.50E-2	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Dinitrogen monoxide	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	NMVOC, non-methane volatile organic compounds, unspecified origin	-	-	kg	5.60E-3	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Methane, fossil	-	-	kg	3.10E-2	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Hydrogen sulfide	-	-	kg	3.00E-6	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Hydrogen chloride	-	-	kg	4.60E-4	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Chlorine	-	-	kg	6.00E-6	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Hydrogen fluoride	-	-	kg	1.20E-5	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Lead	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Fluorine	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 6, update 1999	
	Halogenated hydrocarbons, chlorinated	-	-	kg	1.10E-5	Uncertainty for LCI results cannot be determined, Table 6, update 1999	

	Hydrocarbons, aromatic	-	-	kg	2.80E-5	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Hydrocarbons, aliphatic, alkanes, cyclic	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Aldehydes, unspecified	-	-	kg	4.70E-5	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Cyanide	-	-	kg	4.80E-7	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Sulfate	-	-	kg	4.90E-7	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Hydrogen	-	-	kg	3.20E-3	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Mercury	-	-	kg	1.00E-6	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Ammonia	-	-	kg	4.00E-6	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Carbon disulfide	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Ethane, 1,2-dichloro-	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Ethene, chloro-	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 6, update 1999
	Heat, waste	-	-	MJ	9.81E+1	Uncertainty for LCI results cannot be determined, Table 1, update 1999
water emissions	COD, Chemical Oxygen Demand	-	-	kg	5.10E-2	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	BOD5, Biological Oxygen Demand	-	-	kg	1.20E-3	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Carboxylic acids, unspecified	-	-	kg	6.10E-5	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Solved solids	-	-	kg	1.70E-2	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Hydrocarbons, unspecified	-	-	kg	5.70E-3	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Ammonium, ion	-	-	kg	5.00E-6	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Suspended solids, unspecified	-	-	kg	8.30E-2	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Phenol	-	-	kg	1.20E-5	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Aluminum	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Calcium, ion	-	-	kg	5.40E-2	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Copper, ion	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Iron, ion	-	-	kg	1.00E-6	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Mercury	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Lead	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Magnesium	-	-	kg	1.70E-5	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Sodium, ion	-	-	kg	3.80E-1	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Potassium, ion	-	-	kg	8.20E-4	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Nickel, ion	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Zinc, ion	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Nitrate	-	-	kg	1.00E-6	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Nitrogen	-	-	kg	1.00E-5	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Chromium VI	-	-	kg	2.60E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Chloride	-	-	kg	9.80E-1	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Cyanide	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Fluoride	-	-	kg	1.00E-6	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Sulfate	-	-	kg	8.10E-3	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Carbonate	-	-	kg	1.50E-2	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Phosphate	-	-	kg	9.68E-5	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Arsenic, ion	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Ethane, 1,2-dichloro-	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Ethene, chloro-	-	-	kg	5.00E-7	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Oils, unspecified	-	-	kg	6.90E-5	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Chlorine	-	-	kg	2.40E-5	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Chlorinated solvents, unspecified	-	-	kg	7.20E-5	Uncertainty for LCI results cannot be determined, Table 9, update 1999
	Sulfide	-	-	kg	1.00E-6	Uncertainty for LCI results cannot be determined, Table 9, update 1999

31.4.2 Epoxy resin, disaggregated data

In a second approach we tried to disaggregate as far as possible the updated figures of Boustead (1999). The dataset is made to compare the two possible ways of dealing with cumulative information. The dataset is not meant to be used as a background information in studies as it is not compatible with other LCI data for plastics in this data base.

In some cases it was necessary to rely on information from the pre-version (Boustead 1997). These data have been disaggregated and linked to background data of the database. The following information has been used (tables from the section Ecoprofile Data in Boustead (1999): fuel use (Table 1, energy content of delivered fuel), the feedstock energy (Table 1), the consumption of water resources for processing (Table 5), process specific emissions into water (Table 9) and air (Table 6) and data for wastes associated to the process operations (Table 8).

Important materials like sodium chloride were also considered with their resource use, but not with the requirements for the production, because the latter is included in the aggregated figures for e.g. the energy use. All inputs with a figure <1 mg/kg are assumed to be 0.5 mg/kg. Own assumptions have been used for transports, the type of supply chain for the fuel uses and the waste management. Tab. 31.2 shows the inventory for liquid epoxy resins as it is implemented in the database.

Due to the necessary calculation of inventory entries from cumulative results the data quality is not good.

Tab. 31.2 Disaggregated life cycle inventory for the production of liquid epoxy resin (modified from Boustead 1999).

	Name Location Infrastructure Process Unit	Locatio n	Infrast ructure Unit	epoxy resin, liquid, disaggregated data, at plant	
				RER	0 kg
				0 kg	1.00E+0
output	epoxy resin, liquid, disaggregated data, at plant	RER	0	kg	1.00E+0
resource, in ground	Calcite, in ground	-	-	kg	7.10E-1
	Gas, natural, in ground	-	-	Nm3	6.78E-1
	Oil, crude, in ground	-	-	kg	3.55E-1
	Sand, unspecified, in ground	-	-	kg	1.20E+3
	Sodium chloride, in ground	-	-	kg	1.80E+0
	sylvite, 25 % in sylvinite, in ground	-	-	kg	2.90E-2
resource, in water	Water, well, in ground	-	-	m3	1.40E-5
	Water, river	-	-	m3	9.20E-5
	Water, salt, ocean	-	-	m3	9.50E-4
	Water, cooling, unspecified natural origin	-	-	m3	3.84E-1
	Water, unspecified natural origin	-	-	m3	6.10E-3
technosphere	electricity, medium voltage, production UCTE, at grid	UCTE	0	kWh	2.19E+0
	heavy fuel oil, burned in power plant	RER	0	MJ	1.10E+1
	natural gas, burned in industrial furnace >100kW	RER	0	MJ	5.77E+1
	tap water, at user	RER	0	kg	1.30E+1
	disposal, municipal solid waste, 22.9% water, to sanitary landfill	CH	0	kg	2.98E-1
	disposal, municipal solid waste, 22.9% water, to municipal incineration	CH	0	kg	5.80E-3
	chemical plant, organics	RER	1	unit	4.00E-10
	transport, freight, rail	RER	0	tkm	1.74E+0
	transport, lorry 32t	RER	0	tkm	6.06E+1
emission air, unspecified	Acetaldehyde	-	-	kg	4.70E-5
	Ammonia	-	-	kg	4.00E-6
	Carbon dioxide, fossil	-	-	kg	6.50E-1
	Carbon monoxide, fossil	-	-	kg	2.60E-4
	Halogenated hydrocarbons, chlorinated	-	-	kg	1.10E-5
	Heat, waste	-	-	MJ	7.87E+0
	Hydrocarbons, aromatic	-	-	kg	2.80E-5
	Hydrogen chloride	-	-	kg	2.30E-4
	Hydrogen fluoride	-	-	kg	5.00E-7
	Hydrogen sulfide	-	-	kg	3.00E-6
	Lead	-	-	kg	5.00E-7
	Mercury	-	-	kg	5.00E-7
	Methane, fossil	-	-	kg	2.00E-4
	Methane, chlorotrifluoro-, CFC-13	-	-	kg	8.00E-6
	Nitrogen oxides	-	-	kg	2.70E-3
	Particulates, > 2.5 um, and < 10um	-	-	kg	7.10E-3
	Sulfur dioxide	-	-	kg	1.70E-3
	NMVOCS, non-methane volatile organic compounds, unspecified origin	-	-	kg	4.94E-4
emission water, river	Ammonium, ion	-	-	kg	3.00E-6
	Arsenic, ion	-	-	kg	5.00E-7
	BOD5, Biological Oxygen Demand	-	-	kg	1.10E-3
	Calcium, ion	-	-	kg	5.40E-2
	Carboxylic acids, unspecified	-	-	kg	5.90E-5
	Chloride	-	-	kg	9.80E-1
	Chlorinated solvents, unspecified	-	-	kg	1.13E-4
	Chromium VI	-	-	kg	5.00E-7
	COD, Chemical Oxygen Demand	-	-	kg	5.10E-2
	Copper, ion	-	-	kg	5.00E-7
	Cyanide	-	-	kg	5.00E-7
	DOC, Dissolved Organic Carbon	-	-	kg	1.70E-2
	Fluoride	-	-	kg	1.00E-6
	Oils, unspecified	-	-	kg	6.90E-5
	Hydrocarbons, unspecified	-	-	kg	6.40E-5
	Iron, ion	-	-	kg	1.00E-6
	Magnesium	-	-	kg	1.70E-5
	Mercury	-	-	kg	1.00E-6
	Nickel, ion	-	-	kg	5.00E-7
	Nitrate	-	-	kg	1.00E-6
	Nitrogen	-	-	kg	1.00E-5
	Phenol	-	-	kg	6.00E-6
	Phosphate	-	-	kg	2.20E-4
	Potassium, ion	-	-	kg	8.20E-4
	Sodium, ion	-	-	kg	3.80E-1
	Sulfate	-	-	kg	8.10E-3
	Sulfide	-	-	kg	1.00E-6
	Suspended solids, unspecified	-	-	kg	8.30E-2
	VOC, volatile organic compounds, unspecified origin	-	-	kg	5.20E-3
	Zinc, ion	-	-	kg	5.00E-7

31.4.3 Cast resin insulators

Cast resin insulators are used for different technical equipments. They are produced from epoxy resins, hardeners and a filling material. Fig. 32.2 shows a picture of a cast resin insulator.

Data for the use of energy during the production were not available. Aluminium oxide and dolomite can be used for insulators in SF6 insulated facilities. Quartz powder is another well-known filling material. The filling material is about 46% to 65% of the weight of the produced insulator (Park 1994). A share of 60% is assumed here for the inventory of cast resin insulators. The standard transport distances (100 km lorry, 200 km train) are assumed for the materials.

The life cycle inventory for cast resin insulators is shown in Tab. 31.3. Further information about energy use, emissions and infrastructure were not available.



Fig. 32.31.2 Picture of a cast resin insulator.

Tab. 31.3 Inventory for the production of cast resin insulators from liquid epoxy resin. Sources quoted in the text.

	Name	Location Infrastructure Process Unit	Infrastructure eProces	Unit	epoxy resin insulator (Al ₂ O ₃), at plant	epoxy resin insulator (SiO ₂), at plant	Uncertainty Type Standard deviation95%	GeneralComment
					RER	RER		
					kg	kg		
output	epoxy resin insulator (Al ₂ O ₃), at plant	RER	0	kg	1.00E+0	-		
	epoxy resin insulator (SiO ₂), at plant	RER	0	kg	-	1.00E+0		
technosphere	transport, lorry 32t	RER	0	tkm	1.00E-1	1.00E-1	1	2.09 (4,5,na,na,na,na); Standard distance 100km
	transport, freight, rail	RER	0	tkm	2.00E-1	2.00E-1	1	2.09 (4,5,na,na,na,na); Standard distance 200km
	aluminium oxide, at plant	RER	0	kg	6.00E-1	-	1	1.24 (3,na,1,1,1,5); Estimation based on literature values
	epoxy resin, liquid, at plant	RER	0	kg	4.00E-1	4.00E-1	1	1.24 (3,na,1,1,1,5); Estimation based on literature values
	silica sand, at plant	CH	0	kg	-	6.00E-1	1	1.24 (3,na,1,1,1,5); Estimation based on literature values

31.5 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

31.6 Conclusions

The life cycle inventories presented in this report, can be used in life cycle assessment for complex products where epoxy resins or cast resin insulators are used as materials. But they should not be used for a direct comparison of the materials with other materials, which have been investigated in more detail.

Disaggregating published cumulative life cycle inventory data is a difficult task. The data quality of a study based partly on such cumulative data remains always poor. Using the original cumulative data might lead to neglecting important interventions. Different background data e.g. for transports or energy supply might dominate the outcome of the comparison. Disaggregating data is neither a good solution as it will never be possible to use the same assumptions for direct interventions as in the original study.

Appendices: EcoSpold Meta Information

		epoxy resin, liquid, at plant	epoxy resin, liquid, disaggregated data, at plant	epoxy resin insulator (Al2O3), at plant	epoxy resin insulator (SiO2), at plant
ReferenceFunction	401 Name				
Geography	662 Location	RER 0 kg	RER 0 kg	RER 0 kg	RER 0 kg
ReferenceFunction	493 InfrastructureProcess				
ReferenceFunction	403 Unit				
DataSetInformation	201 Type	1	1	1	1
	202 Version	1.0	1.0	1.0	1.0
	203 energyValues	0	0	0	0
	205 LanguageCode	en	en	en	en
	206 LocalLanguageCode	de	de	de	de
DataEntryBy	302 Person	41	41	41	41
	304 QualityNetwork	1	1	1	1
ReferenceFunction	400 DataSetRelatesToProduct				
	402 IncludedProcesses	Aggregated data for all processes from raw material extraction until delivery at plant	Disaggregated data for all processes from raw material extraction until delivery at plant	Only base materials and transports, direct impacts of processing are not known	Only base materials and transports, direct impacts of processing are not known
	404 Amount	1	1	1	1
	490 LocalName	Epoxyharz, flüssig, ab Werk	Epoxygessharzisolator, Al2O3, ab Werk	Epoxygessharzisolator, SiO2, ab Werk	
	491 Synonyms				
	492 GeneralComment	All data are based on Eco-profiles of the European plastics industry. This dataset is used for methodological comparision in the data base. It shall not be used as background data in LCI.		Rough estimation	Rough estimation
	494 InfrastructureIncluded				
	495 Category	plastics	plastics	plastics	plastics
	496 SubCategory	monomers	monomers	monomers	monomers
	497 LocalCategory	Kunststoffe	Kunststoffe	Kunststoffe	Kunststoffe
	498 LocalSubCategory	Monomere	Monomere	Monomere	Monomere
	499 Formula				
	501 StatisticalClassification				
	502 CASNumber	25928-94-3	25928-94-3		
TimePeriod	601 StartDate	1994	1994	2000	2000
	602 EndDate	1995	1995	2000	2000
	603 DataValidForEntirePeriod	1	1	1	1
	611 OtherPeriodText	Time to which data refer	Time to which data refer	Time of publication	Time of publication
Geography	663 Text	Data for 4 plants in DE, IT, NL, CH	Data for 4 plants in DE, IT, NL, CH	Estimation for RER	Estimation for RER
Technology	692 Text	Production from epichlorohydrin and bisphenol-A	Production from epichlorohydrin and bisphenol-A	manufacturing of insulator	manufacturing of insulator
Representativeness	722 Percent	100	100		
	724 ProductionVolume	190000 Tonnes	190000 Tonnes	not known	not known
	725 SamplingProcedure	Company data	Company data	Estimation	Estimation
	726 Extrapolations	No extrapolation	No extrapolation	none	none
	727 UncertaintyAdjustments	none	none	none	none
DataGenerator AndPublication	751 Person	41	41	41	41
	756 DataPublishedIn	2	2	2	2
	757 ReferenceToPublishedSource	8	8	8	8
	758 Copyright	1	1	1	1
	759 AccessRestrictedTo	0	0	0	0
	760 CompanyCode				
	761 CountryCode				
	762 PageNumbers	chapter epoxy resins	chapter epoxy resins	chapter epoxy resins	chapter epoxy resins

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32 Ethanolamines

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 Review: Heiko Kunst, TU Berlin

32.1 Introduction

In fact, three different substances are summed up in the expression "ethanolamines" - monoethanolamine ($\text{NH}_2\text{-C}_2\text{H}_5\text{O}$, CAS-No. 141-43-5), diethanolamine ($\text{NH-(C}_2\text{H}_5\text{O)}_2$, CAS-No. 111-42-2) and triethanolamine ($\text{N-(C}_2\text{H}_5\text{O)}_3$, CAS-No. 102-71-6). Taking their structure, all three substances are derivatives from ammonia, having one to three $\text{CH}_2\text{-CH}_2\text{-OH}$ groups instead of a single H-atom. While the first and the last one are viscous, colourless, clear liquids at normal room temperature, diethanolamine is a crystalline solid. But all three substances are capable to absorb water and CO_2 from the air and furthermore all of them are miscible with water and alcohols infinitely. The most important chemical and physical properties of the three different ethanolamines used in this inventory are given here. (Frauenkron et al. (2001)).

Tab. 32.1 Chemical and physical properties of the different types of ethanolamines

Property	Value	Mono-ethanolamine	Di-ethanolamine	Tri-ethanolamine	Remarks
Molecular weight	g mol^{-1}	61.08	105.14	149.19	
Density	G cm^{-3}	1.016	1.091	1.125	at 20 °C
Boiling point	°C	170.3	268.5	336.1	at normal pressure
Melting point	°C	10.53	28.0	21.6	at normal pressure

32.2 Reserves and Resources of material

The annual worldwide production capacity in 1999 was about 1.09 Mt per year. Thereof, about one quarter (or 275 kt) is the production capacity of Western Europe – while the most important producers is the United states, responsible for more than 50% of the capacity. For the production of ethanolamines on an industrial scale, only the reaction of ethylene oxide with an excess amount of ammonia is used. Actually, about half of the world production is monoethanolamine, 30 to 35% is diethanolamine and the remaining 15 to 20% triethanolamine.

32.3 Use of material / product

According to Frauenkron et al. (2001), the large scale economical production in large single-lined plants has greatly promoted its use within the different parts of the industry. Today, ethanolamines are used i.e. in the following industrial sectors:

- *Surfactants* – these substances are used widely there as intermediates in the production chain of the different surfactants, used in i.e. as detergent or emulsifier. One of the most important emulsifiers are ethanolamine soaps, produced from fatty acids.
- *Corrosion inhibitor* – in coolants of vehicle engines as well as in drilling or cutting oils, one of the most important component concerning the inhibition of corrosion are diethanolamine and triethanolamine.
- *Gas purification* – again, large amounts of diethanolamine are used for the gas purification from weak acidic components, e.g. hydrogen sulphide or carbon dioxide.

- *Intermediates* – Especially monoethanolamine is used as intermediate for the production of ethylenimine (starting material for an important product in the paper industry) or ethylenediamine (used in agrochemicals).
- *Cement additives* – especially triethanolamine is used since several years as milling additives.

32.4 Systems characterization

In the production process for ethanolamines the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of the different ethanolamines is not considered to be high.

For this inventory, a multi-output process producing all three types is established. According to Frauenkron et al. (2001) is the molar excess of ammonia within the process responsible for the final distribution between the three different types of ethanolamines. Fig. 32.1 shows the product distribution in function of the molar ratio of ammonia and ethyl oxide.

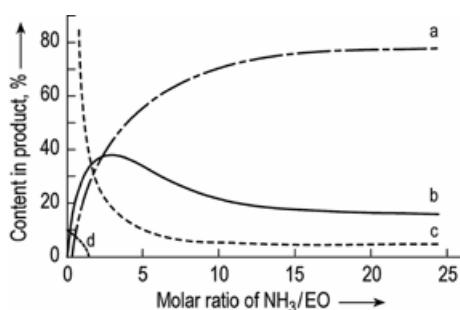


Fig. 32.1 Product distribution of the three different forms of ethanolamines (a= mono, b= di, c= tri) in function of the ratio of ammonia and ethyl oxide (Fig. 1 from Frauenkron et al. (2001))

Based on these information, it is assumed for this study that the molar ratio ammonia/ethyl oxide is 2.5, resulting in 40% mono-, 40% di- and 20% triethanolamine. As process location Europe (RER) is used.

32.5 Ethanolamines, at plant (Location: RER)

32.5.1 Process

This dataset includes a rough estimation of the production process for all three different forms of ethanolamine with the reaction of ethylene oxide and ammonia. Due to missing production data this inventory bases on information given in Frauenkron et al. (2001). The emissions to air and water were estimated using mass balance. It was assumed that wastewater is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is quite large. The process is assessed according to the flow diagram shown in the following figure.

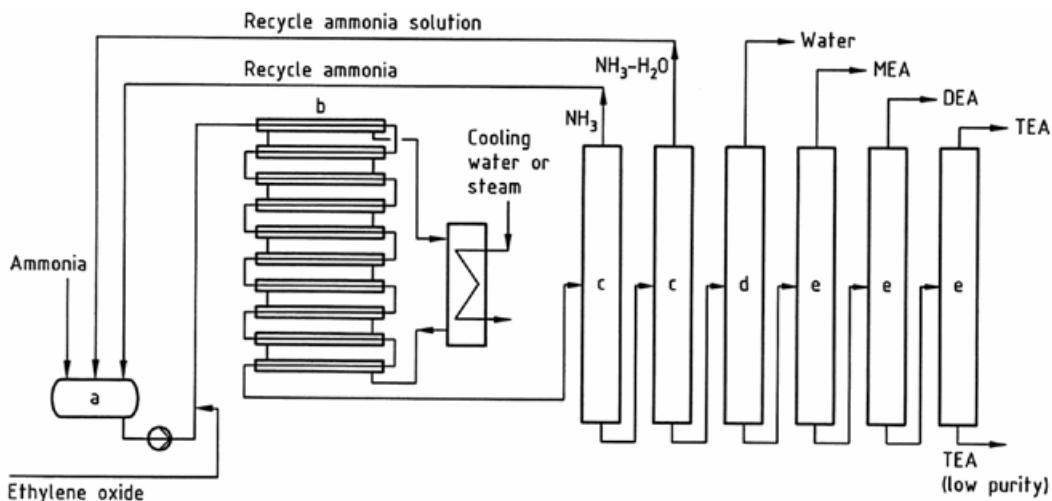
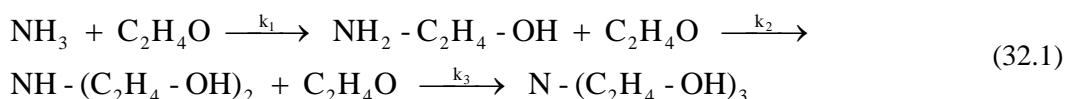


Fig. 32.2 Flow sheet for the production of ethanolamines: a) Aqueous ammonia tank; b) Tubular reactor; c) Ammonia and ammonia solution columns; d) Dehydration column; e) Vacuum fractionation columns (Fig. 2 out of Frauenkron et al. (2001))

The overall reaction for the production of the three different types of ethanolamines can be formulated as follows:



As already mentioned above, the distribution of the products is controlled by an appropriate choice of the ratio between ammonia and ethylene oxide. Actually, pressures up to 16 MPa, reaction temperatures up to 150°C and an excess of ammonia of up to 40 mol per mole ethylene oxide are used in the industry. In all cases, a complete conversion to the three ethanolamines and no significant by-product formation is observed. Thereby the reaction is highly exothermic. All three different reaction steps shown in formula 1.1 have about similar activation energies.

After the reaction, unused ammonia and water are separated from the three ethanolamines by distillation and are recycled within the production circle.

32.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the wastewater treatment. Fossil fuel is needed to generate the desired heat within the process scheme. There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the ethanolamines production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was used. A summary of the values used is given in Tab. 32.2.

Raw materials and Chemicals

For the production of the here assumed 0.4 kg mono-, 0.4 kg di- and 0.2 kg triethanolamine the following stoichiometric inputs are needed (yield 100%):

- ethylene oxide, CH_2OCH_2 : 799.90 g (18.18 mol)
- ammonia, NH_3 : 772.63 g (45.45 mol) – according to the above mentioned ratio of 2.5

For the production, due to the fact that Frauenkron et al. (2001) indicates, that “complete conversion, without significant formation of byproducts (...)" is achieved, a yield of 98% is used in this study. To produce 1 kg ethanolamines according to the above distribution, therefore 816.23 g ethylene oxide and 788.40 g ammonia are considered as raw materials in this inventory.

The process water consumption is not quantified within the examined sources. According to Frauenkron et al. (2001) the ammonia concentration is in the order of 50 to 100% in water. Therefore, a process water input of 0.82 kg per kg product is assumed here. A summary of all values used is given in Tab. 32.2.

Cooling water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the ethanolamines production. According to the ongoing IPPC activities of the European Commission, the cooling water demand may reach 86 kg kWh^{-1} for an once through cooling system, which would lead to a cooling water demand of 48 kg per kg product for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m^3 cooling water per kg product was used.

Transport

Standard distances and means according to Frischknecht et al. (2007) are used for all input materials due to the fact that no information is available in Frauenkron et al. (2001).

32.5.3 Emissions

Waste heat

It was assumed that 100% of the electricity consumed, i.e. 1.2 MJ per kg produced ethanolamines, is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of ethanolamines. As approximation the air emissions occurring from the purge vent, the distillation vent and fugitive emission sources were estimated to 0.2% of the raw material input.

This assumption leads to air emissions of 1.63 g of ethylene oxide and 1.58 g of ammonia per kg produced ethanolamines (according to the distribution mentioned above).

Emissions to water

The remaining amount of unreacted ethylene oxide was assumed to leave the production process with the wastewater. This assumption leads to a pollution of the waste water with 14.7 g ethylene oxide per kg product. Concerning the ammonia, it is assumed that the above shown cycle has a yield of about 98% and therefore only 9.56 g ammonia are found in the wastewater. Further it was assumed that this wastewater is treated in an internal wastewater plant. Therefore, a removal efficiency of 90% for ethylene oxide was assumed, leading to 1.47 g ethylene oxide in the treated water. The carbon contained in the removed ethylene oxide was accounted as CO₂ emissions to air (26.46 g CO₂ per kg product). For the ammonia within the wastewater a removal efficiency for NH₄-N of 70% and for total N of 50% was assumed. The remaining emissions to water were considered as ammonium (NH₄) and nitrate (NO₃). The nitrogen emitted to air (N₂) and remaining in the sewage sludge was neglected. This assumptions leads to emissions of 3.04 g NH₄ and 6.97 g NO₃ per kg product in the treated water. The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of propane in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 32.2.

Solid wastes

Solid wastes occurring during the production of ethanolamines were neglected in this inventory.

Tab. 32.2 Energy demand, resource demand and emissions for the production of ethanolamines

[per kg ethanolamines-mixture]			Remark
INPUTS			
ethylene oxide	kg	0.816	stoichiometric calc., 98% yield
ammonia	kg	0.788	molar ratio of NH ₃ /EtO of 2.5 & 98% yield
Water, unspecified	m3	8.20E-04	estimation, assuming 100% ammonia in water
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m3	2.40E-02	estimation
Transport, by train	tkm	9.63E-01	standard distances & means
Transport, by lorry	tkm	1.60E-01	standard distances & means
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
ethylene oxide, to air	kg	1.63E-03	estimated as 0.2% of input
ammonia, to air	kg	1.58E-03	estimated as 0.2% of input
carbon dioxide, fossil, to air	kg	2.65E-02	from waste water treatment
ethylene oxide, to water	kg	1.47E-03	calculated from mass balance
ammonia (NH ₄ ⁺), to water	kg	3.04E-03	calculated from mass balance
nitrate (NO ₃ ⁻), to water	kg	6.97E-03	calculated from mass balance
COD, BOD	kg	2.13E-02	calculated from water emissions
TOC, DOC	kg	8.02E-03	calculated from water emissions

32.5.4 Infrastructure

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg ethanolamines was included.

32.5.5 Allocation

As this is a multioutput process, resulting in three different products, an allocation has to be established for the above described environmental loads (inputs, outputs). Due to a lack of further informations, a simple allocation according to the mass is established here, resulting in allocation factors of 0.4 for mono- and diethanolamine and of 0.2 for triethanolamine. This allocation factor is used for all inputs and outputs except the input of ethylene oxide. As this input is calculated from stoichiometry, the allocation is done according to the respective consumption of ethylene oxide per product - resulting in factors of 36.0% for mono-, 41.9% for di- and 22.1% for triethanolamine.

32.6 Data quality considerations

The following table shows the data quality indicators for the inventory of the ethanolamines production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the ethanolamines production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data.

Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 32.9.

Tab. 32.3 Input / Output, allocation factors and uncertainty values for the process “ethanolamines, at plant (RER)”

Explanation	Name	Location	Unit	ethanolamine s, production		standardDeviation95%	GeneralComment	monoethanolamine, at plant	diethanolamine, at plant	triethanolamine, at plant
				RER 0	kg					
				uncertaintyType						
Resource Input from Technosphere	Water, cooling, unspecified natural origin	RER	m3	2.40E-02	1	1.88	(5.5.1.1.4.5); estimated with data from a large chem. plant	40	40	20
	Water, unspecified natural origin		m3	8.20E-04	1	1.21	4.(n.a.n.a,n.a,n.a); estimation based on process yield 90-99.8%	40	40	20
	ethylene oxide, at plant		kg	8.16E-01	1	1.21	4.(n.a.n.a,n.a,n.a); estimation based on process yield 90-99.8%	36	41.9	22.1
	ammonia, liquid, at regional storehouse		kg	7.88E-01	1	1.21	4.(n.a.n.a,n.a,n.a); estimation based on process yield 90-99.8%	40	40	20
	electricity, medium voltage, production UCTE, at grid		kWh	3.33E-01	1	1.88	(5.5.1.1.4.5); estimated with data from a large chem. plant	40	40	20
	heat, natural gas, at industrial furnace >100kW		MJ	2.00E+00	1	1.88	(5.5.1.1.4.5); estimated with data from a large chem. plant	40	40	20
	chemical plant, organics		unit	4.00E-10	1	3.77	(4.5.1.3.5.4); estimation	40	40	20
	transport, freight, rail		tkm	9.63E-01	1	2.09	(4.5.n.a.n.a,n.a); standard distances	40	40	20
Output	transport, lorry 32t		tkm	1.60E-01	1	2.09	(4.5.n.a.n.a,n.a); standard distances	40	40	20
	monoethanolamine, at plant	RER	kg	0.4				100	0	0
	diethanolamine, at plant	RER	kg	0.4				0	100	0
Air emission Water emission	triethanolamine, at plant	RER	kg	0.2				0	0	100
	Heat, waste	Water emission	MJ	1.20E+00	1	1.88	(5.5.1.1.4.5); calculated from electricity input	40	40	20
	Carbon dioxide, fossil		kg	2.65E-02	1	1.88	(5.5.n.a.n.a,4.5); estimated from mass balance and WWTP effic.	40	40	20
	Ethylene oxide		kg	1.63E-03	1	2.32	(5.5.n.a.n.a,5); estimation	40	40	20
	Ammonia		kg	1.58E-03	1	2.32	(5.5.n.a.n.a,5); estimation	40	40	20
	BOD5, Biological Oxygen Demand		kg	2.13E-02	1	2.11	(5.5.n.a.n.a,4.5); estimated from mass balance and WWTP effic.	40	40	20
	COD, Chemical Oxygen Demand		kg	2.13E-02	1	2.11	(5.5.n.a.n.a,4.5); estimated from mass balance and WWTP effic.	40	40	20
	DOC, Dissolved Organic Carbon		kg	8.02E-03	1	2.11	(5.5.n.a.n.a,4.5); estimated from mass balance and WWTP effic.	40	40	20
Water emission	TOC, Total Organic Carbon		kg	8.02E-03	1	2.11	(5.5.n.a.n.a,4.5); estimated from mass balance and WWTP effic.	40	40	20
	Ethylene oxide		kg	1.47E-03	1	2.11	(5.5.n.a.n.a,4.5); estimated from mass balance and WWTP effic.	40	40	20
	Ammonium, ion		kg	3.04E-03	1	2.11	(5.5.n.a.n.a,4.5); estimated from mass balance and WWTP effic.	40	40	20
	Nitrate		kg	6.97E-03	1	2.11	(5.5.n.a.n.a,4.5); estimated from mass balance and WWTP effic.	40	40	20

32.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

32.8 Conclusions

The inventory for the different ethanolamines is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if one of these ethanolamines is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of these materials with other, alternative products.

32.9 EcoSpold Meta Information

ReferenceFunction	Name	ethanolamines, production
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Ethanolamine-Produktion, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The multioutput process "ethanolamines, at plant" delivers the co-products "monoethanolamine, at plant", "diethanolamine, at plant" and "triethanolamine, at plant". An allocation to the three products is done by using the mass, resulting in monoethanolamine 40%, dimethanolamine 40% and trimethanolamine 20%. Large uncertainty of the process data due to weak data on the production process and missing data on
ReferenceFunction	CASNumber	
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from ethylene oxide and ammonia with a process yield of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	1.1 Mt worldwide in 1999, thereof 275 kt in
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

32.10 References

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- Frischknecht et al. (2007) Frischknecht R., Althaus H.-J., Doka G., Dones R., Hischier R., Hellweg S., Jungbluth N., Kellenberger D., Nemecek T., Rebitzer G. and Spielmann M. (2007) Overview and Methodology. Final report ecoinvent Data v2.0 No. 1. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.
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33 Ethylenediamine

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33.1 Introduction

Ethylenediamine ($C_2H_8N_2$, CAS-No. 107-15-3) – also called EDA or 1,2-diaminoethane – is at room temperature a colourless liquid. Ethylenediamine is infinitely miscible with water, methanol, acetone, benzene, diethyl ether – but only slightly soluble in lower hydrocarbons. For this inventory the functional unit is 1 kg liquid ethylenediamine. The most important chemical and physical properties of ethylenediamine used in this inventory are given here.

Tab. 33.1 Chemical and physical properties of ethylenediamine (according to Eller & Henkes (2000))

Property	Unit	Value	Remarks
Molecular weight	60.1	$g\ mol^{-1}$	
Boiling point	117	°C	at normal pressure
Melting point	10.9	°C	at normal pressure

33.2 Reserves and Resources of material

The production of ethylenediamine is made out of ammonia that reacts either with ethylene dichloride, monoethanolamine or with ethylene oxide (for more details see chapter 33.4). Therefore, all further discussion of resources equals to the discussion about the oil / gas reserves (see energy-report) esp. about ammonia (see ammonia, chapter 11, within this report here).

33.3 Use of material / product

According to Eller & Henkes (2000), ethylenediamine are used in a variety of different fields – e.g. in detergents, resins, crop protection agents, paper chemicals, lubricants or pharmaceutical products. One of the most important products out of ethylenediamine is EDTA – especially in the United States.

In 1998, the worldwide production capacity of ethylenediamine was in the order of 340 kt. Thereof, 250 kt have been consumed within the same year – whereof the European market represents about 100 kt. The major producers are Union Carbide, Dow, AkzoNobel, Tosch, BASF and Bayer (Eller & Henkes (2000)).

33.4 Systems characterization

In the production process for ethylenediamine the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of ethylenediamine is not considered to be high. For this inventory the functional unit is 1 kg of liquid ethylenediamine. As process location Europe (RER) is used.

According to Eller & Henkes (2000), three principal possibilities – starting from three different educts – for the production of ethylenediamine can be distinguished:

- *Ethylene dichloride (EDC) process:* EDC is treated with aqueous or liquid ammonia at 100°C in the liquid phase. Occuring by-products are DETA (diethylenetriamine), TETA (triethylenediamine)

- and, as an unavoidable by-product, amine hydrochloride. For the neutralization of the latter one, caustic soda, lime or other bases are used. The product – ethylenediamine – is extracted from the aqueous stream by extraction or by distillation methods.
- *Monoethanolamine process*: Here, the educt reacts with ammonia and hydrogen over a catalyst at about 20 MPa and 150 to 230°C. Occurring by-products in this reaction are e.g. DETA and piperazine. The yield of EDA is in the order of 75% - based on an ethanolamine conversion of 93%.
 - *Ethylene oxide process*: Ethylene oxide is reacted with ammonia. Occurring by-products in this production scheme are DETA, piperazine and di- and triethanolamine.

Actually, almost two third of all ethylenediamine production sites use the first mentioned production technique – the EDC process. Having in mind the very weak data availability of the production of ethylenediamine, for this study only the first of these three reactions is taken into account.

33.5 Ethylenediamine, at plant (Location: RER)

33.5.1 Process

This dataset includes a rough estimation of the production process for ethylenediamine. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The mentioned production way for ethylenediamine, based on EDC can be summarized within the following overall stoichiometric reaction equation:



According to Eller & Henkes (2000), the further products of this reaction are higher oligomers (e.g. diethylenetriamine) and amine hydrochloride. The latter one has to be neutralized with a base – usually either soda or lime – to form sodium resp. calcium chloride. Therefore, for this study the following reaction equation is used as basis for all further calculations:



33.5.2 Resources

Energy

There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the ethylenediamine production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 33.2.

Raw materials and Chemicals

According to the above shown final reaction equation - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of ethylenediamine:

- Ethylene dichloride, C₂H₄Cl₂: 1646.76 g (16.639 mol)
- ammonia, NH₃: 565.72 g (33.278 mol)
- sodium hydroxide, NaOH: 1331.02 g (33.278 mol)

For the production a yield of 95% for the overall reaction is assumed. Therefore 1733.427 g ethylene dichloride, 595.499 g ammonia and 1401.068 g sodium hydroxide are considered as raw materials in this inventory. A summary of the values used is given in Tab. 33.2.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the ethylenediamine production.

For the process water amount, due to a lack of data, an amount of 50% of the cooling water amount is assumed here – leading to an input of 12 kg water per kg ethylenediamine.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of 4 * 10⁻¹⁰ units per kg ethylenediamine was included.

33.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg ethylenediamine is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of ethylenediamine. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input (EDC and ammonia, but not of sodium hydroxide).

This assumption leads to air emissions of 3.467 g ethylene dichloride and 1.191 g ammonia.

Emissions to water

The remaining amount of unreacted raw materials was assumed to leave the production process with the wastewater. This assumption leads to a pollution of the waste water with 83.204 g EDC, 28.584 g

of ammonia and 70.05 g of sodium hydroxide per kg product. Additionally, the in the reaction produced amount of 1944.759 g sodium chloride is also found within the waste water output.

Further it was assumed that this wastewater is treated in a internal wastewater plant. Therefore, a removal efficiency of 90% for EDC was assumed, leading to 8.32 g EDC in the treated water. The carbon contained in the removed EDC was accounted as CO₂ emissions to air (66.584 g CO₂ per kg product). Ist content of chloride was together with the produced sodium chloride as well as the sodium hydroxide assumed to be dissolved in the waste water, leading to an emission of 1235.08 g Cl⁻ and 803.57 g Na⁺ to the surface water (river). For the ammonia within the waste water a removal efficiency for NH₄-N of 70% and for total N of 50% was assumed. The remaining emissions to water were considered as ammonium (NH₄) and nitrate (NO₃). The nitrogen emitted to air (N₂) and remaining in the sewage sludge was neglected. This assumption leads to emissions of 9.08 g NH₄ and 20.849 g NO₃ per kg product in the treated water. The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of propene in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 33.2.

Solid wastes

Solid wastes occurring during the production of ethylenediamine were neglected in this inventory.

Tab. 33.2 Energy demand, Resource demand and emissions for the production of ethylenediamine.

[per kg ethylenediamine]			Remark
INPUTS			
ethylene dichloride	kg	1.733	stoichiometric calc., 95% yield
ammonia	kg	0.595	stoichiometric calc., 95% yield
sodium hydroxide	kg	1.401	stoichiometric calc., 95% yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m ³	2.40E-02	estimation
Water, unspecified	m ³	1.20E-02	estimation
transport by train	tkm	2.24E+00	standard distances
transport by lorry, 32t	tkm	3.73E-01	standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
ethylene dichloride, to air	kg	3.47E-03	estimated as 0.2% of input
ammonia, to air	kg	1.19E-03	estimated as 0.2% of input
carbon dioxide, fossil, to air	kg	6.66E-02	from waste water treatment
ethylene dichloride, to water	kg	8.32E-03	calculated from mass balance
ammonia, NH4+, to water	kg	9.08E-03	calculated from mass balance
nitrate, NO ₃ -, to water	kg	2.08E-02	calculated from mass balance
chloride ions, to water	kg	1.24E+00	calculated from mass balance
sodium ions, to water	kg	8.04E-01	calculated from mass balance
COD, BOD	kg	7.75E-03	calculated from water emissions
TOC, DOC	kg	2.02E-03	calculated from water emissions

33.6 Data quality considerations

The following table shows the data quality indicators for the inventory of ethylenediamine production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the ethylenediamine production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data.

Tab. 33.3 Input / Output and uncertainty for the process “ethylenediamine, at plant (RER)”

Explanation	Name	Location	Unit	ethylenediamine, at plant		standard deviation 95 %	uncertainty type	General Comment			
				RER							
				0	kg						
Resource	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant				
Input from Technosphere	Water, unspecified natural origin		m3	1.20E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant				
Input from Technosphere	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	1.40E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%				
	ethylene dichloride, at plant	RER	kg	1.73E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%				
Input from Technosphere	ammonia, liquid, at regional storehouse	RER	kg	5.95E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%				
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant				
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant				
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation				
	transport, freight, rail	RER	tkm	2.24E+00	1	2.09	(4,5,na,na,na,na); standard distances				
	transport, lorry 32t	RER	tkm	3.73E-01	1	2.09	(4,5,na,na,na,na); standard distances				
Output	ethylenediamine, at plant	RER	kg	1							
Air emission	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input				
	Carbon dioxide, fossil		kg	6.66E-02	1	1.88	(5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Ethane, 1,2-dichloro-		kg	3.47E-03	1	2.32	(5,na,na,na,5); estimation				
	Ammonia		kg	1.19E-03	1	2.32	(5,na,na,na,5); estimation				
Water emission	BOD5, Biological Oxygen Demand		kg	7.75E-03	1	2.11	(5,na,na,4,5); estimated from mass balance and WWTP effic.				
	COD, Chemical Oxygen Demand		kg	7.75E-03	1	2.11	(5,na,na,4,5); estimated from mass balance and WWTP effic.				
	DOC, Dissolved Organic Carbon		kg	2.02E-03	1	2.11	(5,na,na,4,5); estimated from mass balance and WWTP effic.				
	TOC, Total Organic Carbon		kg	2.02E-03	1	2.11	(5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Chloride		kg	1.24E+00	1	2.11	(5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Sodium, ion		kg	8.04E-01	1	3.55	(5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Ethane, 1,2-dichloro-		kg	8.32E-03	1	3.55	(5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Ammonium, ion		kg	9.08E-03	1	2.11	(5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Nitrate		kg	2.08E-02	1	2.11	(5,na,na,4,5); estimated from mass balance and WWTP effic.				

33.7 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

33.8 Conclusions

The inventory for ethylenediamine is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if ethylenediamine is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

33.9 EcoSpold Meta Information

ReferenceFunction	Name	ethylenediamine, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Ethylenediamine, ab
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid ethylenediamine. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	107-15-3
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from ethylene dichloride and ammonia at elevated temperature and subsequent neutralization of the by-products by sodium hydroxide. The overall process yield is of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

33.10 References

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34 Ethylene Dichloride

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Review: Heiko Kunst, TU Berlin

34.1 Introduction

This chapter describes the production of ethylene dichloride. This chemical is also known under its abbreviation EDC or as 1,2-dichloroethane. EDC is used primarily for the production of vinyl chloride monomer (VCM), a precursor for the production of the plastic polyvinyl chloride or PVC. There are both integrated EDC / VCM plants as well as stand-alone EDC plants.

34.2 Reserves and resources of EDC

EDC, $C_2H_2Cl_2$, is a chlorinated organic chemical compound. It is generated from ethylene and chlorine, either directly or by using hydrogen chloride. Major manufacturers include Solvay, Norsk Hydro, Dow Chemical, PPG Industries and Elf Atochem, among many others (Wells, 1999).

34.3 Characterisation of EDC

EDC is a highly volatile liquid with a melting point of – 35.4 °C and a boiling point of 83.7 °C. It is toxic and flammable. It is a dangerous fire and explosion hazard. ECD is miscible with most chlorinated organics and most organic solvents (Wells, 1999).

34.4 Production and use of EDC

EDC is produced industrially by the chlorination of ethylene, either directly with chlorine or by using hydrogen chloride (HCl). In practice, both routes are carried out together, the HCl stems from the cracking of EDC to vinyl chloride. HCl from other processes can also be used. The major outlet is for the production of vinyl chloride monomer (VCM). There are both integrated EDC / VCM plants as well as stand-alone EDC plants.

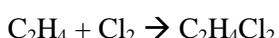
In 1997, European production of EDC was 9.4 million tons, according to (IPPC Chemicals, 2002). This makes it Europe's most produced halogenated product. Global demand is expected to grow at roughly 6% per year in the short run, while future growth depends on the global demand for PVC. Major plants with capacities greater than 600'000 tons per year are located in Belgium, France, the Netherlands, Italy, Norway, the US, Canada, Brazil, Saudi Arabia, Japan and Taiwan, according to (Wells, 1999).

34.5 System characterization

Available data from production sites often refer to the entire EDC/VCM chain and do not differentiate between the production lines. There is some information on stand-alone sites, however, and this data forms the basis for part of the inventory developed in this report.

EDC can be produced by two routes, both involving the chlorination of ethylene. One route involves direct chlorination, the other is carried out with hydrochloric acid (HCl) and oxygen. In practice, both routes are carried out together.

34.5.1 EDC by direct chlorination of ethylene (Wells, 1999)



Raw materials per ton

- Ethylene 295 kg
- Chlorine 735 kg

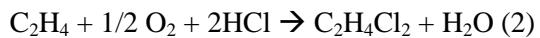
Yield on ethylene 96-98% / on chlorine 98%

Liquid chlorine and pure ethylene are reacted in the presence of a catalyst (ferric chloride). The chlorination reaction can be carried out at low or high temperature. In the low-temperature process takes place at 20 °C – 70 °C. The reaction is exothermic and heat exchangers are needed. The advantage of this process is that there are few by-products.

The high-temperature process takes place at 100 °C – 150 °C. The heat generated is used to distill the EDC, which conserves energy.

According to (IPPC Chemicals, 2002), the reaction product consists of more than 99% EDC, the rest being chlorinated hydrocarbons that are removed with the light ends and then combusted or sold.

34.5.2 EDC by chlorination and oxychlorination (Wells, 1999)



Raw materials per ton (Wells)

- Ethylene 302 kg
- HCl 760 kg

Yield on ethylene 93-97% / on HCl 96-99%

Pure ethylene and hydrogen chloride are heated and mixed with oxygen. The reaction occurs at 200 °C – 300 °C at 4-6 bar in the presence of a catalyst (cupric chloride). After reaction the gases are quenched with water. The acid and water are removed, the gases are cooled and the organic layer is washed and dried. If air is used instead of oxygen, the reaction is easier to control. However, oxygen-based processes operate at lower temperatures, reducing vent gas volume. By-products are ethyl chloride, 1,1,2-trichloromethane and chloral (trichloroacetaldehyde).

34.5.3 Thermal cracking of EDC (IPPC Chemicals, 2002)

Thermal cracking of dry, pure EDC produces VCM and HCl. Often all the HCl generated in the cracking section is reused in producing EDC by oxychlorination. Plants that exhibit this characteristic and also do not export EDC are called “balanced”. The balanced process is the common process used as a Best Available Technology benchmark.



34.6 Life cycle Inventory for EDC

Specific data for stand-alone EDC plants are hard to come by, as most data refer to integrated production of EDC and VCM. This report assumes that half of the EDC is produced at stand-alone sites and half is produced at integrated EDC/VCM plants that are not balanced, i.e. EDC is exported.

34.6.1 Precursor materials (IPPC Chemicals, 1992)

In balanced units, ethylene and chlorine are generally supplied by pipeline from nearby facilities. HCl can be provided by an external source. EDC can be shipped in as well, but care needs to be taken as to its purity. In this report, it is assumed that the precursors are supplied by pipeline, and that no additional HCl is needed.

It is assumed that half of the EDC is produced by direct chlorination in a stand-alone plant. Raw materials per ton according to (Wells, 1999):

- Ethylene 295 kg
- Chlorine 735 kg

It is furthermore assumed that half of the EDC is produced by oxychlorination. Raw materials per ton EDC according to (IPPC Chemicals, 2002):

- Ethylene 302 kg
- Chlorine 760 kg

It is assumed that all plants are air based. Raw materials per ton EDC according to (APME 2002):

- Ethylene 306 kg
- Chlorine 714 kg

These latter values are based on information provided by eight EDC producers and do not differentiate between the oxychlorination and chlorination routes. An average of all three sources is taken as the basis for this report, i.e. Ethylene 301 kg and Chlorine 736.3 kg.

34.6.2 Energy usage

The direct chlorination and oxychlorination of ethylene are highly exothermic. There is heat recovery and steam generation at the oxychlorination plant. Energy consumption for stand-alone EDC plants is “minor”, when the high-temperature chlorination process is used. APME (2002) reports that an average of 0.38 MJ of electricity, 1.8 MJ of fuels and 0.044 kg (0.12 MJ) of steam are used in the production of 1 kg of EDC.

It is further assumed that the heat generated by reaction is used to distill all the EDC produced by the various reactions (Wells, 1999).

Oxygen-based processes will also use electricity for the separation of oxygen from air. This usage is included in the oxygen inventory.

34.6.3 Air emissions

Little is given on stand-alone EDC plants as most information pertains to EDC/VCM plants. Emission sources include losses from flanges, valves, decoupling of tanks, etc. Emissions from stacks connected

to air pollution control devices are generally low, according to (IPPC Chemicals, 2002, Chapter 12.4.2).

Tab. 34.1 Air emission factors for EDC production (g/kg)

Substance	IPPC Chemicals, (2002) *	Table 52 (APME 2002)
NOx	0.020 (approx.)	0.030
CO	0.008	0.006
CO ₂	23.8 ***	26
SO ₂	ng	0.005
dust	ng	0.160
EDC	0.0001	0.051
NM VOC	0.065 ***	ng
Hydrocarbons	ng	0.340
HCl	0.0015 **	0.021
Methane	ng	0.079
Ethylen	ng	0.012
VCM	ng	0.006
Dioxins, related compounds***	ng	ng

* value used in this report except where ng or for EDC

** stand-alone EDC production

*** Note: emissions stemming from the thermal cracking of EDC to VCM are allocated to VCM. Emissions attributed to EDC may also stem from the incineration of liquid process wastes.. Most of the volatile organics generated during cracking of EDC to VCM are captured with recovered HCl and routed back to the oxychlorination stage. This plant produces EDC and VCM with a mass ratio of 1.19:1. According to (CMR11-25-02) the price ratio of EDC to VCM is about 1:2. Therefore, the emissions arising from integrated production are allocated 40.5% to EDC and 59.5% to VCM.

**** The oxychlorination process generates dioxin-related compounds, notably octo-chlorodibenzofuran. No emission figures are given⁶. These substances typically adhere to spent catalyst and are found in the heavy-end residues of EDC distillation and in the catalyst residues.

34.6.4 Wastewater emissions (IPPC Chemicals, 2002)

The production and use of EDC is regulated by EC Directive 90/415/EEC, which stipulates EDC releases equal to or less than 5 g / ton VCM production.

Washwater and condensate from EDC purification contains VCM, EDC and other chlorinated hydrocarbons such as chloral or chloroethanol, as well as other organics such as sodium formate glycol, and chloroform. Moreover, effluents also contain dioxin-related compounds, which adhere to catalyst particles. The presence of these compounds is influenced by the oxychlorination process technology.

34.6.5 Liquid wastes (IPPC Chemicals, 2002)

Liquid wastes stem from the EDC distillation unit. The residues are a mix of light ends (chlorinated C₁ and C₂ hydrocarbons with a boiling point lower than EDC) and heavy ends (e.g. chlorinated aromatics or cyclic hydrocarbons). Dioxin-related compounds formed by the oxychlorination reactions adhere to catalyst residues in metal sludge.

Direct chlorination does not result in significant quantities of wastes. In stand-alone EDC plants the liquid residues generated by the direct chlorination process are generally less than 5 kg / to EDC. Oxychlorination can result in a range of values, depending on process parameters. Typically, 24 to 40 kg /

⁶ However, the European Council of Vinyl Manufacturers has set an emission limit of 0.1 ng / Nm³

ton VCM of residues are produced. Because of the high chlorine content, the residues are treated either by high-temperature incineration (produces HCl, which is either recycled or sold) or used as feedstock for high-temperature chlorination of a hydrocarbon (produces CCl₄ or other highly chlorinated hydrocarbons).

Tab. 34.2 Wastewater (values after treatment) (IPPC Chemicals, 2002)

Substance	Emission as kg/t EDC	Source	Type of plant
EDC	0.00005	table 12.11, plant 5a	Stand-alone
AOX	0.0002	"	"
COD	0.0005	"	"
Chlorinated hydrocarbons*	0.7	Table 12.15	integrated
Dioxins	1 µg 1-TEQ TCDD / Tonne EDC from oxy-chlorination	"	"
Copper	1 mg / ton EDC **	"	"

* VCM + EDC + chloromethanes + trichloroethane + others before biological treatment

** only for oxychlorination with fluidised bed. As there are no numbers available on the prevalence of the production routes, a 50:50 split chlorination/oxychlorination is assumed. Therefore, 0.5 mg of copper ions are emitted with wastewater per ton of produced EDC.

34.6.6 Solid wastes (IPPC Chemicals, 2002)

The main solid wastes are spent catalyst (from the oxychlorination process), direct chlorination residues and sludge from wastewater treatment. The catalysts may be contaminated with dioxins. Amounts are given according to (IPPC Chemicals, 2002, Chapter 12.3.5)

- Spent **oxychlorination** catalyst (10-200 g / to VCM – no figures available for EDC production). The spent catalyst is found in heavy ends and in wastewater purification sludge. (IPPC Chemicals, 2002) Chapter 12.4.3 indicates that 100 µg or 0.1 mg of dioxin-like compounds (1-TEQ TCDD) are produced per ton of EDC. A report indicates that wastewater sludge that has been flocculated has a concentration of about 500 µg 1-TEQ TCDD / kg (sludge) – see Chapter 12.4.3 in (IPPC Chemicals, 2002). Based on the above figures, it can be assumed that an average of 100 g spent oxychlorination catalyst are produced per ton of VCM. Since no average figures are available on integrated EDV/VCM plants that produce EDC, the same split is assumed as in 1.6.3. Therefore, the emissions arising from integrated production are allocated 40.5% to EDC and 59.5% to VCM. It is therefore assumed that 40.5 g of spent catalyst stem from EDC production by oxychlorination. Using the same split, it can further be assumed that 40.5 µg 1-TEQ TCDD adhere to the spent catalyst. This report further assumes that half of the EDC is produced by the oxychlorination route, half by the chlorination route (with no significant dioxin emissions as the catalyst used is not copper-based and presumably does not catalyze dioxin formation). Total solid waste per ton of produced EDC is therefore on the order of 20.3 g spent catalyst containing 20.3 µg 1-TEQ TCDD. This type of catalyst typically contains about 5.5 % copper. This entails that 1.1 g of copper are contained in the 20.3 g spent catalyst per ton of EDC.
- **Direct chlorination** residues: inorganic iron salts, 10 – 50 g / to VCM (again, no figures available on stand-alone EDC plants). It is assumed that 30 g of iron chloride are disposed of per ton of VCM. The same split as above is assumed, leaving 6 g of iron chloride per ton of EDC to be disposed of. No dioxin is assumed to be formed with this process route.

The wastes are usually disposed of in hazardous waste landfills or incinerated in a hazardous waste incinerator. This report assumes a 50:50 split.

34.6.7 Infrastructure and transports

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.0000000004 units per kg of produced EDC.

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007b) are used for the different raw materials.

34.7 Data quality considerations

The data quality is considered to be good, as the values taken from literature stem from actual measured values. The fuels input data are in part an approximation, although the energy usage is monitored, as are the amounts of precursor substances.

The following table summarizes the input and output data as well as the uncertainties used for the production of EDC. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 34.10.

Tab. 34.3 Input / output data and data quality for EDC production in Europe

Explanations	Name	Location	Unit	ethylene dichloride, at plant	Uncertainty Type	Standard Deviation 95%	General Comment
	Location			RER			
	Infrastructure Process			0			
	Unit			kg			
Input from Technosphere	chemical plant, organics	RER	unit	4.00E-10	1	1.31	(2,2,1,2,3,5); infrastructure of a typical plant
	chlorine, liquid, production mix, at plant	RER	kg	7.35E-01	1	1.31	(2,2,1,2,3,5); precursor compound
	copper, at regional storage	RER	kg	2.30E-05	1	1.15	(1,4,1,1,1,4); copper catalyst used in the chlorination process
	ethylene, average, at plant	RER	kg	2.95E-01	1	1.31	(2,2,1,2,3,5); precursor compound
	transport, freight, rail	RER	tkm	6.00E-01	1	1.32	(3,5,1,1,1,5); estimates taken from the quality guidelines
	transport, lorry 32t	RER	tkm	1.00E-01	1	1.32	(3,5,1,1,1,5); estimates taken from the quality guidelines
	AOX, Adsorbable Organic Halogen as Cl	-	kg	2.00E-07	1	1.15	(1,4,1,1,1,4); one plant producing EDC
Water emissions	BOD5, Biological Oxygen Demand	-	kg	5.00E-07	1	1.15	(1,4,1,1,1,4); one plant producing EDC
	Chlorinated solvents, unspecified	-	kg	5.00E-08	1	1.15	(1,4,1,1,1,4); one plant producing EDC
	COD, Chemical Oxygen Demand	-	kg	5.00E-07	1	1.15	(1,4,1,1,1,4); one plant producing EDC
	Copper, ion	-	kg	1.00E-09	1	1.15	(1,4,1,1,1,4); copper catalyst used in the chlorination process
	Copper	-	kg	2.30E-05	1	1.15	(1,4,1,1,1,4); copper catalyst used in the chlorination process
	Carbon dioxide, fossil	-	kg	2.90E-02	1	1.15	(1,4,1,1,1,4); one plant producing EDC
	Carbon monoxide, fossil	-	kg	8.00E-06	1	1.15	(1,4,1,1,1,4); one plant producing EDC
Soil emission	Halogenated hydrocarbons, chlorinated	-	kg	1.00E-07	1	1.15	(1,4,1,1,1,4); one plant producing EDC
	Hydrogen chloride	-	kg	1.50E-06	1	1.15	(1,4,1,1,1,4); one plant producing EDC
	Nitrogen oxides	-	kg	2.00E-05	1	1.15	(1,4,1,1,1,4); one plant producing EDC
	NMVOC, non-methane volatile organic compound	-	kg	6.50E-05	1	1.15	(1,4,1,1,1,4); one plant producing EDC
	ethylene dichloride, at plant	RER	kg	1			
Outputs							

34.8 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

34.9 Conclusions

The inventory for EDC is based on literature, representing the actual production situation in Europe. The dataset is in accordance with the present quality guidelines of the ecoinvent project. The data are thus of a quite good quality and can be used in a broad context.

34.10 EcoSpold Meta Information

ReferenceFunction	Name	ethylene dichloride, at
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Cradle-to-gate, all precursor compounds, transports included
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Ethyldichlorid, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	This inventory is a split if the available data on the two production routes: oxychlorination and chlorination.
ReferenceFunction	CASNumber	
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	
Technology	Text	The values are a mix over surveyed plants in Europe in the given time period.
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

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35 Ethylene Glycol

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35.1 Introduction

This chapter describes the production of ethylene glycol. This chemical is also known as glycol, mono ethylene glycol (MEG), ethylene alcohol or as 2-hydroxyethanol. MEG is used primarily for the production of polyester resins for fibres, films, laminates and polyethylene terephthalate (PET) soft drink bottles. Another major use for ethylene glycol is as antifreeze.

35.2 Reserves and resources of glycol

MEG is a hydrocarbon compound with two hydroxy (alcohol) groups. It is produced from the hydration of ethylene oxide (see chapter 36). Major manufacturers include Hoechst Celanese, Shell Chemical and Union Carbide, among many others (Wells, 1999).

35.3 Characterisation of glycol

MEG is a clear colourless liquid with a freezing point of – 12.6 °C and a boiling point of 197.3 °C. It is a stable, non-corrosive liquid. This chemical is very hygroscopic (will take up water) and reacts strongly with ethers and oxidizing agents. Ethylene glycol is classified as harmful by the EC Hazardous Substances directive. It is soluble in water, ethyl alcohol and ethers. (Wells, 1999).

35.4 Production and use of glycol

Ethylene is directly oxidized with air or oxygen in the presence of a catalyst to ethylene oxide (EO). The ethylene oxide is subsequently treated with water (hydrolyzed) and forms a variety of glycols, most notably mono ethylene glycol (MEG), di ethylene glycols (DEG) and tri ethylene glycols (TEG). About 40% of all European EO production is converted into glycols, globally the figure is about 70% (IPPC Chemicals 2002). Usually, EO and MEG are produced together at integrated plants.

There is a broad range of applications for ethylene glycol. Over half of the glycol is used for the production of polyester fibres, while PET production accounts for another fifth (Wells, 1999). When combined with corrosion inhibitors, it is used as antifreeze in automobiles, pumps and industrial heating and cooling equipment. Films and resins consume another 10% of ethylene glycol production. Other applications are as a humectant (moisture absorbing agent), as a plasticizer and as a softening agent (Wells 1999).

DEG is used in the fibre industry and as a tobacco humectant while TEG is used in the manufacture of cellophane for food packagin (IPPC Chemicals, 2002)

No direct production figures were available. However, based on the available figures for ethylene oxide production in (IPPC Chemicals 2002), it can be assumed that approximately 5 million tons of ethylene oxide were converted to glycols in Europe and the U.S. in 1997 (7 million tons of glycols based on the ration of molecular weights of MEG to EO). Further production capacity of at least 1.2 million tons is reported from Saudi Arabia, Kuwait and South Korea (Wells, 1999), giving a total of ca. 8.5 million tons of ethylene glycols production worldwide.

35.5 System characterization

An ethylene oxide / water mixture is heated up to 190 - 200°C and pressurized to 14-22 bar. According to (IPPC Chemicals 2002), about 70 – 95% of the mixture consists of MEG, the rest primarily consisting of DEG and TEG. (Wells 1999) gives a yield for MEG of 67%. Poly-ethylene glycols are also formed, but can be controlled by using an excess of water. According to (IPPC Chemicals, 2002), the usual configuration for glycols production is an integrated EO / EG plant.

IPPC Chemicals (2002) also indicates that the glycol products typically consists of 70 – 95% w/w of MEG, the primary co-product being DEG, some of which can further react to TEG. All of the EO feed is converted into MEG, DEG TEG as well as some heavy glycols, which may however be incinerated. 2 – 100 kg heavy glycols / ton EO can be produced.



- (1) production of ethylene oxide
- (2) production of MEG from EO and water
- (3) production of DEG from EO and MEG
- (4) production of TEG from EO and DEG

The water-glycol mixture is fed to multiple evaporators, where water is recovered and recycled. The water-free glycol mixture is separated by fractional distillation. Acids (e.g. 1% sulfuric acid) catalyse the hydration reaction and allow lower temperatures to be used.

35.6 Life cycle Inventory for glycol

EO / glycols plants can be designed to produce glycols only, ethylene oxide only or a mix of glycols and EO. In practice, the last configuration is usually implemented, because MEG is the most important outlet for EO. Specific data for glycols production only are hard to come by, as most data refer to integrated production of ethylene oxide and glycols (IPPC Chemicals 2002).

Tab. 35.1 Processes and outputs associated with formaldehyde production

Inventory name	ID number	Description
Ethylene glycol, at plant	1210	Production of monoethylene glycol (MEG)
Ethylene oxide, in ethylene glycol plant	5900	Multi-output process that produces 1210, 5901, 5902
Diethylene glycol, at plant	5901	Coprodut from MEG production (DEG)
Triethylene glycol, at plant	5902	Coprodut from MEG production (TEG)

35.6.1 Precursor materials

It is assumed that an average 82.5% of the glycols consists of MEG. This report assumes that a further 10% is DEG, the remainder being TEG and heavy glycols. Some 35 kg of heavy glycols are produced per ton of ethylene oxide.

Tab. 35.2 Raw materials for EG production

Amounts in kg	IPPC Chemicals (2002)	Price \$/ lb, tanks, based on (CMR11-25-02)	Price x mass allocation factor (%)
Input: - Ethylene oxide	703		
Output: - MEG	825	0.25	85
- DEG	100	0.17	7
- TEG	40	0.48	8
- Heavy glycols	35	ng	ng

35.6.2 Energy usage

The EO/EG process is both a consumer and a producer of energy. The EO section is typically a steam producer, the glycols section uses heat for dewatering. (IPPC Chemicals, 2002). No values are given. Catalyst selectivity and the relative size of the EO and EG parts determine if a plant is a net energy producer or importer. Since each European plant has different characteristics, it is difficult to give a meaningful range of energy figures (IPPC).

It must be assumed that some steam is utilized for glycol distillation. No figures are given. Electrical energy consumption is given as 0.377 kWh / kg in (BUWAL 232).

35.6.3 Air emissions

Little is given on stand-alone EG plants as most information pertains to EO plants. It is assumed that the emissions pertain to total output (1000 kg glycols):

- Ethylene 0.006 kg / to EG
- Acetaldehyde 0.0014 kg / to EG

Taken from (IPPC Chemicals, 2002), table 9.9, point sources

35.6.4 Wastewater emissions

- TOC: 0.2 kg / ton EG

Value is taken from IPPC Chemicals (2002): Table 9.10. The reduction efficiency for TOC of the wastewater treatment plant is 60-70%, according to Table 9.11 of IPPC Chemicals (2002). This would amount to 0.07 kg TOC / ton glycol (post-treatment values). It is assumed that the emissions pertain to total output (1000 kg glycols).

In IPPC Chemicals (2002), Chapter 9.3.5 further makes reference to a plant producing 2.3 tons of TOC with an annual production of 2273 tons of glycol, which amounts to 1 kg TOC / kg glycol, probably a pre-treatment value (not specified).

An emission factor given in Table 9.12 lists an unspecified liquid emission with heavy glycols and salts as 0.03 kg / ton of product. The effluent stems from glycol purification.

35.6.5 Liquid wastes (IPPC Chemicals, 2002)

Besides heavy glycols that may not be sold to customers, no further mentionis made of liquid wastes. Such wastes are incinerated and produce energy.

35.6.6 Solid wastes (IPPC Chemicals, 2002)

None given, as spent catalysts are associated with ethylene oxide production.

35.6.7 Infrastructure

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.000000004 units per kg of produced glycols.

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

35.7 Data quality considerations

The data quality is considered to be good, as the values taken from literature stem from actual measured values. The fuels input data are in part an approximation, although the energy usage is monitored, as are the amounts of precursor substances.

The following table summarizes the input and output data as well as the uncertainties used for the production of ethylene glycols. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 35.10.

Tab. 35.3 Input / output data and data quality for ethylene glycols production in Europe

Explanations	Name	Location	Unit	ethylene oxide, in ethylene glycol plant	Uncertain ty Type	Standard Deviation 95%	General Comment	diethylen	ethylene	triethylen	
								RER	RER	RER	
								kg	kg	kg	
Resources	Water, unspecified natural origin	m3	6.00E-03	1	1.88	5,5,1,1,4,5); estimated with data from a large chem. plan	7	85	8		
Input from Technosphere	chemical plant, organics	RER unit	4.00E-10	1	1.22	(2,2,1,2,1,5); infrastructure	7	85	8		
	electricity, medium voltage, production UCTE, at grid	UCTE	3.77E-01	1	1.22	(2,2,1,2,1,5); power usage	7	85	8		
	ethylene oxide, at plant	RER	kg	7.03E-01	1	1.22	(2,2,1,2,1,5); precursor	7	85	8	
air emission	Heat, waste	-	MJ	1.35E+00	1	1.30	(4,2,1,2,1,5); waste heat	7	85	8	
	Acetaldehyde	-	kg	1.40E-06	1	1.22	(2,2,1,2,1,5); emission	7	85	8	
	Ethene	-	kg	6.00E-06	1	1.22	(2,2,1,2,1,5); emission	7	85	8	
water emission	BOD5, Biological Oxygen Demand	-	kg	2.88E-04	1	1.22	(2,2,1,2,1,5); emission	7	85	8	
	COD, Chemical Oxygen Demand	-	kg	2.88E-01	1	1.22	(2,2,1,2,1,5); emission	7	85	8	
	DOC, Dissolved Organic Carbon	-	kg	7.50E-05	1	1.22	(2,2,1,2,1,5); emission	7	85	8	
	TOC, Total Organic Carbon	-	kg	7.50E-05	1	1.22	(2,2,1,2,1,5); emission	7	85	8	
Outputs	diethylene glycol, at plant	RER	kg	0.1				100	0	0	
	ethylene glycol, at plant	RER	kg	0.825				0	100	0	
	triethylene glycol, at plant	RER	kg	0.04				0	0	100	

35.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

35.9 Conclusions

The inventory for ethylene glycols is based on literature, representing the actual production situation in Europe. The datasets are in accordance with the present quality guidelines of the ecoinvent project. The data are thus of a quite good quality and can be used in a broad context.

35.10 EcoSpold Meta Information

ReferenceFunction	Name	ethylene oxide, in ethylene glycol plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	includes precursors, transports and infrastructure
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Ethylenoxid, in Ethyleneglykolfabrik
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	This Multi-Output inventory is based on literature sources that are based on actual plant throughputs and measurements. The oxidation of ethylene oxide leads to three coproducts: ethylene glycol, diethylene glycol (DEG) and triethylene glycol (TEG).
ReferenceFunction	CASNumber	
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	RER
Technology	Text	represents a current cross-section of actual plants in Europe
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	see technology
Representativeness	UncertaintyAdjustments	none

35.11 References

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36 Ethylene oxide

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36.1 Introduction

This chapter describes the production of ethylene oxide (EO). This chemical is also known as oxirane, dihydro-oxirene or dimethylene oxide or as 1,2-epoxyethane. EO is used primarily for the production of ethylene glycol and its production is frequently integrated with that of its major derivative (see chapter ethylene glycol).

36.2 Reserves and resources of EO

Ethylene oxide is a hydrocarbon compound made from ethylene and oxygen. Major manufacturers include Hoechst Celanese, Shell Chemical, and Union Carbide, among many others (Wells, 1999).

36.3 Characterisation of EO

EO is a colourless liquid or gas with a freezing point of – 112.6 °C and a boiling point of 10.4 °C. It is toxic, flammable and very reactive. This chemical is a classified suspected human carcinogen. Its vapor will cause permanent damage to the eyes and respiratory tract. Ethylene oxide gas or liquid mixed with air or an inert gas can decompose explosively. EO is highly flammable and its vapor will decompose violently at high temperatures. It is soluble in water, ethyl alcohol and many organic solvents. (Wells, 1999).

36.4 Production and use of EO

Ethylene is directly oxidized with air or oxygen in the presence of a catalyst to ethylene oxide (EO). About 40% of all European EO production is converted into glycols, globally the figure is about 70% (IPPC Chemicals 2002). Usually, EO and MEG are produced together at integrated plants.

There is a broad range of applications for ethylene oxide. Over half of the EO produced worldwide is converted to ethylene glycols. The next most important outlet is the production of ethoxylates, used as surfactants in detergents (Wells 1999).

EO is also used to produce ethanolamines, used as a chemical intermediary and in surfactants. Other products are glycol ethers, a solvent for paints, and di- and triethylene glycols. EO is also an excellent disinfectant and sterilizing agent.

Industrial production started in 1937 with a union Carbide process based on ethylene and air. In 1958 oxygen rather than air was introduced by Shell Development Company, and today most processes are based on oxygen (IPPC Chemicals 2002).

Total European production was 3.4 million tons per year in 1997, while the US produced 5.2 million tons per year. Further production capacity of at least 1.2 million tons is reported from Saudi Arabia, Kuwait, Japan and South Korea (Wells, 1999), giving a total of at least 9.8 million tons of ethylene oxide production worldwide.

36.5 System characterization

EO is produced by passing a mixture of ethylene and oxygen over a solid silver-containing catalyst. Selectivity is improved by the addition of chlorine compounds such as chloroethane. Reaction condi-

tions are temperatures of about 200 - 300 °C and a pressure of 10 – 30 bar (Wells, 1999). The main by-products are carbon dioxide and water, formed when ethylene is fully oxidised or some of the EO is further oxidised. Ethylene glycols are formed when the reactor gases are absorbed into chilled water.



- (1) production of ethylene oxide
- (2) production of MEG from EO and water
- (3) production of carbon dioxide and water from oxidation of ethylene

The carbon dioxide is removed from the scrubber by absorption with hot aqueous potassium carbonate, the resulting solution is steam stripped to remove the carbon dioxide, which is vented to air. The potassium carbonate is regenerated. The carbon dioxide can be reused for inerting, or is sold, or is vented to atmosphere.

36.6 Life cycle Inventory for EO

EO / glycols plants can be designed to produce glycols only, ethylene oxide only or a mix of glycols and EO. In practice, the last configuration is usually implemented, because MEG is the most important outlet for EO. (IPPC Chemicals, 2002). Although glycols can be formed when EO reacts with water, the by-product formation was not quantified in available literature and hence is not accounted for here.

36.6.1 Precursor materials (IPPC Chemicals, 2002)

There is a range of consumption of the raw materials ethylene and oxygen (or air), depending on the catalyst used:

Tab. 36.1 Raw materials for EO production (IPPC Chemicals, 2002)

Consumption in kg/ ton of ethylene oxide produced	Oxygen-based process	Air-based process
Ethylene	750 - 850	800-900
Oxygen	750-1100	

It is assumed that 50% of the ethylene oxide is produced by either route (825 kg of ethylene and 462.5 kg oxygen). (Wells 1999) gives much higher values but a lower yield (60% for the air-based process instead of the 70 – 80% mentioned in (IPPC Chemicals, 2002). The yield is low because of uncontrolled reaction of ethylene to form carbon dioxide and water.

36.6.2 Energy usage

The formation of EO is highly exothermic and produces steam, which is circulated to the EO recovery section (Wells, 1999). Additional steam import may be necessary. Steam production depends on EO catalyst selectivity. Low catalyst selectivity gives higher heat release (presumably because of the full

oxidation of ethylene to carbon dioxide and water, which is more exothermic than the reaction to EO), while high catalyst selectivity will conversely lead to higher steam imports. Since each plant has different characteristics, it is difficult to give a valid range of values. Data in (IPPC Chemicals 2002) Table 9.8 are given for a 160 kt/year EO plant, which requires 3-4 kg steam / kg product. Typically, the EO production is a net steam producer. This study assumes that an average plant does not require steam import.

Electrical power usage is not specified. However, a value can be approximated from a large chemical plant site in Germany producing 2.05 Mt per year (intermediates included) of different chemicals (Gendorf 2000). For this inventory an amount of 1.2 MJ / kg electricity was used.

36.6.3 Air emissions

In many cases, emissions are combusted or treated catalytically, so that the contribution of process-based emissions is difficult to quantify.

Tab. 36.2 VOC emissions from ethylene oxide production (IPPC Chemicals, 2002)

Air pollutant (kg/ton pro- duct)	Air- based plants	Oxygen- based plants	Newer plants (un- specified process)	Newer plants, point source (unspecified process)	This re- port
Ethane	6*	3*	ng	ng	ng
Ethylene	92*	0.1-2.5*	0.1	0.14 – 0.3	0.23
Ethylene*	92	0.1-2.5	ng	ng	"
Ethylene oxide	1*	0.5*	2.6 ***	0.001 – 0.038	0.02
Methane			0.08	0.25 – 1.3	0.08
Ethylene and methane		0 – 3.1**			ng
Total HC		0** - 16			ng
NMVOC				0.18 – 0.3	0.24
CO				0.11	0.11

* 1990 pre-treatment figures (these values do not enter Ecoinvent)

** when vent gases are oxidized

*** losses from storage tanks in the absence of abatement

Most VOC emissions are normally fugitive (valves, flanges) and from maintenance or inspections. They may also stem from small leaks in cooling systems as well as storage tank breathing losses and displacement.

No emission factor for CO₂ is given, but (IPPC Chemicals, 2002) does mention a plant that produced 80'000 tons of EO in 1998. A nearby gas producer used part of the CO₂ by-product and an estimated 16'566 tons were released. Using this example, it can be estimated that up to 0.21 kg CO₂ / kg EO are released to the atmosphere.

36.6.4 Wastewater emissions (IPPC Chemicals, 2002)

Effluent from the EO recovery section may contain 1 – 20 kg TOC / ton EO before treatment. Assuming the stream can be mixed with other effluent and treated biologically (removal efficiency 90%), the resulting post-treatment values are 0.1 – 2 kg TOC / ton EO. The specific TOC content of process effluent (post-treatment, as above) is 0.01 – 0.4 kg TOC / ton EO. Post-treatment COD values are given as 0.18 – 0.2 kg / ton EO.

36.6.5 Liquid wastes (IPPC Chemicals, 2002)

None given

36.6.6 Solid wastes (IPPC Chemicals, 2002)

The main solid wastes are spent catalyst. Values are given as 0.12 – 0.8 kg / ton EO. The catalyst is sent to reclaimers for the silver catalyst content and is then landfilled. It is assumed that 0.5 kg catalyst base is landfilled per ton of ethylene oxide.

36.6.7 Infrastructure and transports

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.0000000004 units per kg of EO.

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

36.7 Data quality considerations

The data quality is considered to be good, as the values taken from literature stem from actual measured values. The fuels input data are in part an approximation, although the energy usage is monitored, as are the amounts of precursor substances.

The following table summarizes the input and output data as well as the uncertainties used for the production of ethylene oxide. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 36.10.

Tab. 36.3 Input / output data and data quality for EO production in Europe

Explanations	Name	Location	Unit	ethylene oxide, at plant	Uncertainty Type	Standard Deviation 95%	General Comment
	Location		RER				
	Infrastructure Process		0				
	Unit		kg				
Input from Technosphere	chemical plant, organics disposal, catalyst base Eth.oxide prod., 0% water, to residual material landfill	RER	unit	4.00E-10	1	1.22	(2,2,1,2,1,5); infrastructure of a typical plant (4,2,1,2,1,5); disposal of catalyst base
	electricity, medium voltage, production UCTE, at grid	CH	kg	5.00E-04	1	1.30	(4,2,1,2,1,5); electricity
	ethylene, average, at plant	UCTE	kWh	3.30E-01	1	1.30	(2,2,1,2,1,5); precursor
	oxygen, liquid, at plant	RER	kg	8.25E-01	1	1.22	(2,2,1,2,1,5); precursor
	transport, freight, rail	RER	kg	4.63E-01	1	1.22	(2,2,1,2,1,5); precursor
	transport, lorry 32t	RER	tkm	5.41E-01	1	1.24	(2,4,1,2,1,5); transport
		RER	tkm	1.05E-01	1	1.24	(2,4,1,2,1,5); transport
water emission	BOD5, Biological Oxygen Demand	-	kg	1.90E-04	1	1.22	(2,2,1,2,1,5); emissions
	COD, Chemical Oxygen Demand	-	kg	1.90E-04	1	1.22	(2,2,1,2,1,5); emissions
	DOC, Dissolved Organic Carbon	-	kg	2.00E-04	1	1.22	(2,2,1,2,1,5); emissions
	TOC, Total Organic Carbon	-	kg	2.00E-04	1	1.22	(2,2,1,2,1,5); emissions
air emission	Heat, waste	-	MJ	1.20E+00	1	1.30	(4,2,1,2,1,5); emissions
	Carbon dioxide, fossil	-	kg	2.10E-01	1	1.22	(2,2,1,2,1,5); emissions
	Carbon monoxide, fossil	-	kg	1.10E-04	1	1.22	(2,2,1,2,1,5); emissions
	Ethene	-	kg	2.30E-04	1	1.22	(2,2,1,2,1,5); emissions
	Ethylene oxide	-	kg	2.00E-05	1	1.22	(2,2,1,2,1,5); emissions
	Methane, fossil	-	kg	7.50E-04	1	1.22	(2,2,1,2,1,5); emissions
	NMVOCS, non-methane volatile organic compounds, unspecified origin	-	kg	2.40E-04	1	1.22	(2,2,1,2,1,5); emissions
Outputs	ethylene oxide, at plant	RER	kg	1			

36.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

36.9 Conclusions

The inventory for EO is based on literature, representing the actual production situation in Europe. The dataset is in accordance with the present quality guidelines of the ecoinvent project. The data are thus of a quite good quality and can be used in a broad context.

36.10 EcoSpold Meta Information

ReferenceFunction	Name	ethylene oxide, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Precursors, transports, infrastructure.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Ethylenoxid, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The processes that are used to produce ethylene oxide from ethylene, oxygen or air are described in this inventory. These processes also produce carbon dioxide in some quantity.
ReferenceFunction	CASNumber	75-21-8
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	RER
Technology	Text	represents a current cross-section of actual plants in Europe
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	see technology
Representativeness	UncertaintyAdjustments	none

36.11 References

- Frischknecht et al. (2007) Frischknecht R., Althaus H.-J., Doka G., Dones R., Hischier R., Hellweg S., Jungbluth N., Kellenberger D., Nemecek T., Rebitzer G. and Spielmann M. (2007) Overview and Methodology. Final report ecoinvent Data v2.0 No. 1. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.
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37 Fleece

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37.1 Introduction

The following explications are based mainly on the respective chapter in Weibel & Stritz (1995).

According to the mentioned report, it is in principle possible to use glass fibre or plastics fibre as starting material for the fleece production. For this study here, a polyester fleece with an average weight of 200 to 400 g/m² is used – actually a typical kind of fleece used e.g. as sound absorber or as support for sealing tracks.

37.2 Reserves and Resources of material

The production of Fleece is made out of different materials like glass fibres or different types of plastics fibres. Therefore, all further discussion of resources can be found within the respective chapters of e.g. the report about plastics or construction materials (Hischier (2007), Kellenberger et al. (2007)).

37.3 Systems characterization

The quantitative information for the production process of Fleece is based mainly on information from one Swiss producer and are representative for the beginning of the 90s. This company represents 55% of the Swiss market and declares that the production situation abroad is similar. In fact, the remaining 45% of the used fleece in Switzerland are produced in the surrounding countries.

For this inventory the functional unit is 1 kg of Fleece. As process location Europe (RER) is used. Thus, the module here represents only a first estimation of the process requirements on a European level and should be used accordingly.

According to Weibel & Stritz (1995), the used raw material follows the following steps: opening of fibres, mixing, pile creation, pile deposition and feeding, needling, transport, cutting and rolling. Furthermore the fleece is heated to about 220°C resulting in a thermal solidification. For a separation of the different tracks, a mechanical cutter is used. The final packaging into cartonboard and plastics film is done manually.

37.4 Fleece, at plant (Location: RER)

37.4.1 Resources

Raw materials and Chemicals

According to Weibel & Stritz (1995), the production of 1 kg of Fleece requires the materials summarized in Tab. 37.1. These values are based on the information from one Swiss producer and are valuable for the production situation in the beginning of the 90s (see also remarks in chapter 37.3). Due to a lack of more recent information, these data are still used within this study here.

Tab. 37.1 raw material and chemicals consumption for the production of 1 kg Fleece (data from Weibel & Stritz (1995))

Input	Amount	Unit	Remarks
chemicals	5.50E-03	kg	shown as "chemicals organic, unspecified"
concrete binder	7.00E-04	kg	shown as "cement unspecified"
cartonboard	2.40E-02	kg	shown as "coreboard"
PE film	2.30E-02	kg	shown as "packaging film, LDPE"
polyester and copolyester	1.10E+00	kg	shown as "polyethylene, high density (HD-PE)"

Actually, for the production polyester and copolyester is used as raw material in unknown amounts. Due to a lack of specific data, the data from high density polyethylene are used for both of them, similar to Weibel & Stritz (1995). The error due to this is according to this data source small.

Energy

According to Weibel & Stritz (1995), the production of 1 kg of Fleece requires the different energy carriers and amounts for the different production steps as summarized in Tab. 37.2. These values are based on the information from one Swiss producer and are valuable for the production situation in the beginning of the 90s (see also remarks in chapter 37.3). Due to a lack of more recent information, these data are still used within this study here.

Tab. 37.2 energy consumption for the production of 1 kg Fleece (data from Weibel & Stritz (1995))

Input	Amount	Unit	Remarks
propene as fuel	2.23E+00	MJ	shown as "heat, natural gas, at industrial furnace >100kW"
electricity	8.64E-01	MJ	shown as UCTE mix

Water use

In weibel1995 is no information about the water consumption. As the material is heated, it is assumed in this study, that there is also a cooling system integrated further on in the production process. Therefore, in order not to neglect the cooling water demand of the process, this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the Fleece production.

For the process itself, it is assumed that no water is used.

Transport and Infrastructure

According to Weibel & Stritz (1995), the production of 1 kg of Fleece is connected with the transport amounts summarized in Tab. 37.3. These values represent the amount produced by the only Swiss producer as well as the imports from the surrounding countries and represent the situation in the beginning of the 90s (see also remarks in chapter 37.3). Due to a lack of more recent information, these data are still used within this study here.

Tab. 37.3 transport efforts for the production of 1 kg Fleece (data from Weibel & Stritz (1995))

Input	Amount	Unit	Remarks
transport on the road	1.45E-01	tkm	shown as "transport, lorry 32t"

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg Fleece was included.

37.4.2 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air / water

In Weibel & Stritz (1995) no process specific emissions to air or to water are mentioned – only a reference to the emissions included in the fuels is made. In addition it is mentioned, that a part of the unspecified organic chemicals is emitted into air, but no quantitative information is available therefore. In this study, it is assumed that 5% of the used chemicals is emitted into air as various hydrocarbons.

Solid wastes

According to Weibel & Stritz (1995), the production of 1 kg of Fleece results in a production of 0.1 kg of the raw material – here polyethylene. In this study the dataset “disposal, polyethylene, 0.4% water, in municipal waste incineration” is used therefore. Further waste is not mentioned and therefore not taken into account.

37.5 Data quality considerations

Tab. 37.4 shows the data quality indicators for the inventory of Fleece production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the Fleece production has a quite high uncertainty, because they are out of date (representing the beginning of 90s) and based on a different geographical area (one Swiss company, used as representative for European average). Higher uncertainties exist for the cooling water demand and the air emission. Due to missing data its values are based mainly on assumptions and approximations. Also for the infrastructure only an approximation was used because of missing data. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes.

Tab. 37.4 Input / Output and uncertainty for the process “Fleece, PE, at plant (RER)”

Explanation	Name	Location	Unit	fleece, polyethylene, at plant	UncertaintyType	StandardDeviation95%	GeneralComment
				RER 0 kg			
				Infrastructure Process Unit			
Resources Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. Plant
	chemicals organic, at plant	GLO	kg	5.50E-03	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company
	packaging film, LDPE, at plant	RER	kg	2.30E-02	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company
	cement, unspecified, at plant	CH	kg	7.00E-04	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company
	core board, at plant	RER	kg	2.40E-02	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company
	polyethylene, HDPE, granulate, at plant	RER	kg	1.10E+00	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.23E+00	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	2.40E-01	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company
	transport, lorry 32t	RER	tkm	1.45E-01	1	2.12	(2,4,3,3,3,5); data from 1 Swiss company
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation
	disposal, polyethylene, 0.4% water, to municipal incineration	CH	kg	1.00E-01	1	1.35	(2,4,3,3,3,5); data from 1 Swiss company
	fleece, polyethylene, at plant	RER	kg	1			
Output Air emission	Heat, waste		MJ	8.64E-01	1	1.35	(2,4,3,3,3,5); calculated from electricity input
	Hydrocarbons, aliphatic, alkanes, unspecified		kg	2.75E-04	1	2.32	(5,5,na,na,na,5); estimation

37.6 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

37.7 Conclusions

An average European dataset for the production of polyethylene vlies for the year 2000 is established. The dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on a former LCI report about construction materials. The dataset of PE vlies is based on information from one Swiss company and refers to the beginning of 1990s. The data are thus of a reasonable quality and can be used in quite a broad context.

37.8 EcoSpold Meta Information

ReferenceFunction	Name	fleece, polyethylene, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, energy consumption and waste amounts from a company. Infrastructure of the plant as an approximation.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Vlies, Polyethylen, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represents 1 kg of fleece out of polyethylene
ReferenceFunction	CASNumber	
TimePeriod	StartDate	1993
TimePeriod	EndDate	1995
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	time to which data refer
Geography	Text	data from 1 Swiss company are used for the European average
Technology	Text	technology used within Europe in the beginning of the 90s
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	Process data based on data from 1 Swiss company, used here as average data for European situation.
Representativeness	Extrapolations	see geography
Representativeness	UncertaintyAdjustments	none

37.9 References

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38 Fluorine

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Summary

This section investigates the production of fluorine as a basic product for SF₆. It is a rough and incomplete inventory, which is based on information found in the literature. The main impacts arise from the use of electricity and due to the production of the raw material hydrogen fluoride. The inventory of fluorine production can be used for the assessment of this raw material in connection with the production of SF₆.

38.1 Introduction

Fluorine (CAS 7782-41-4) is investigated as an intermediate product for the production SF₆.

38.2 Resources for Fluorine

In all modern fluorine-production units, the gas is produced by electrolysis of KF· 2HF (solution of potassium fluoride in anhydrous hydrogen fluoride with 40.68 wt % HF) (Jaccaud et al. 1999). Potassium salts are used to produce the potassium fluoride.

38.3 Use of Fluorine

The world's production of elemental fluorine, except for countries with planned economies, is concentrated in seven countries with an overall capacity of ca 17'000t/a. It is mainly used in two areas: manufacture of UF₆ (18'000- 21'000t/a corresponding to 6'000 – 7'000t of F) and direct manufacture of 5'100 – 7'700t/a of SF₆, corresponding to 4'000 – 6'000t of F. The rest is required for miscellaneous applications (Jaccaud et al. 1999).

38.4 System Characterisation

Elemental fluorine production units are integrated into SF₆ and UF₆ production units to avoid transport difficulties (Jaccaud et al. 1999).

38.5 Life Cycle Inventory

For this inventory it is assumed that pure HF is the only raw input because data for KF were not available. The electricity consumption is 14 – 17kWh/kg F₂ and the efficiency is 90 – 95% (Jaccaud et al. 1999). The inventory is calculated with 15.3kWh/kg electricity and an efficiency of 92.5% (mean values with logarithmic deviation).

Liquid effluents from the production facilities contain diluted hydrofluoric acid, and have to be treated as well as the flue gases from the process (Jaccaud et al. 1999). However, exact emission data and quantities are not known. It is assumed that 1kg/t of hydrogen fluoride is emitted to the air. Transports and infrastructure are estimated with generic data. Other impacts are not accounted for in the inventory. The unit process raw data and data quality indicators are shown in the following table.

Tab. 38.1 Unit process raw data and data quality indicators for fluorine production.

	Name	Location Infrastructure	Process Unit	Infr ast ruc tur ePr	Unit	fluorine, liquid, at plant	Uncertainty Type	StandardDe viation95%	GeneralComment
output	fluorine, liquid, at plant			RER	0	kg	1.00E+0		
technosphere	hydrogen fluoride, at plant			GLO	0	kg	1.14E+0	1	2.03 (3,4,2,3,5,na); Estimation for the use of KF · 2HF (40.68 wt % HF) with pure HF, 92.5% yield
	chemical plant, organics			RER	1	unit	4.00E-10	1	3.90 (5,na,1,1,5,na); Rough estimation
	electricity, medium voltage, production UCTE, at grid			UCTE	0	kWh	1.53E+1	1	1.10 Range from literature
	transport, freight, rail			RER	0	tkm	6.83E-1	1	2.09 (4,5,na,na,na,na); Standard distance 600km
	transport, lorry 32t			RER	0	tkm	1.14E-1	1	2.09 (4,5,na,na,na,na); Standard distance 100km
emission air, unspecified	Heat, waste			-	-	MJ	5.50E+1	1	1.10 Range from literature
	Hydrogen fluoride			-	-	kg	1.00E-3	1	1.77 (5,na,na,na,1,na); Estimation

38.6 Data Quality Considerations

The simplified approach with a pedigree matrix has been used for calculating the standard deviation.

38.7 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

38.8 Conclusions

The inventory of fluorine production can be used for the assessment of this raw material in connection with the production of e.g. SF₆.

Appendices: EcoSpold Meta Information

ReferenceFunction	401 Name	fluorine, liquid, at plant
Geography	662 Location	RER
ReferenceFunction	493 InfrastructureProcess	0
ReferenceFunction	403 Unit	kg
DataSetInformation	201 Type	1
	202 Version	1.0
	203 energyValues	0
	205 LanguageCode	en
	206 LocalLanguageCode	de
DataEntryBy	302 Person	41
	304 QualityNetwork	1
ReferenceFunction	400 DataSetRelatesToProduct	1
	402 IncludedProcesses	Production of fluorine from hydrogenc fluoride. Infrastructure estimated with generic data. Data for raw material KF were not available.
	404 Amount	1
	490 LocalName	Fluor, flüssig, ab Werk
	491 Synonyms	
	492 GeneralComment	This module investigates the production of fluorine as a basic product for SF6. It is a rough and incomplete inventory which is based on information found in the literature.
	494 InfrastructureIncluded	1
	495 Category	chemicals
	496 SubCategory	inorganics
	497 LocalCategory	Chemikalien
	498 LocalSubCategory	Anorganika
	499 Formula	F2
	501 StatisticalClassification	
	502 CASNumber	7782-41-4
TimePeriod	601 StartDate	1999
	602 EndDate	1999
	603 DataValidForEntirePeriod	1
	611 OtherPeriodText	Time of publication
Geography	663 Text	Estimation for Europe
Technology	692 Text	Electrolysis of KF-2HF (40.68 wt % HF)
Representativeness	722 Percent	
	724 ProductionVolume	17000 t/a worldwide
	725 SamplingProcedure	Literature survey
	726 Extrapolations	From single data.
	727 UncertaintyAdjustments	none
DataGenerator AndPublication	751 Person	41
	756 DataPublishedIn	2
	757 ReferenceToPublishedSource	8
	758 Copyright	1
	759 AccessRestrictedTo	0
	760 CompanyCode	
	761 CountryCode	
	762 PageNumbers	chapter fluorine

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39 Formaldehyde

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39.1 Introduction

This chapter describes the production of formaldehyde. This chemical is also known as methylene oxide, methyl aldehyde, formic aldehyde and other terms. Formaldehyde is used primarily for the production of resins and adhesives for plywood and particleboard production.

39.2 Reserves and resources of formaldehyde

Formaldehyde is an organic chemical compound. It is generated from methyl alcohol, either from an aqueous solution or by oxidation with air. Major manufacturers include BASF, Bayer, Du pont, Perstorp and Elf Atochem, among many others (Wells, 1999).

39.3 Characterisation of formaldehyde

Formaldehyde (CH_2O , CAS-No. 50-00-0, Mr 30.03) is a colorless gas at ambient temperature that has a pungent, suffocating odor and polymerizes in the presence of acids or alkali agents. It is very soluble in water (55 g/100 mL). The most important chemical and physical properties of formaldehyde are given in Tab. 39.1.

The liquid and gas polymerize readily at low and ordinary temperatures up to 80 °C. It is a skin, eye and mucous membrane irritant (IPPC Chemicals, 2002). Formaldehyde is toxic and a suspected carcinogen at high concentrations, and is also a moderate fire risk.

Tab. 39.1 Chemical and physical properties of formaldehyde

Property	Value	Unit
Molecular weight	30.0262	g mol^{-1}
Vapor density	1.03	
Boiling point	-19.5	°C
Melting point	-118	°C
Density of the liquid	0.8153 (at -20 °C) 0.9172 (at -80 °C)	g/cm^3

39.4 Production and use of formaldehyde

Formaldehyde is produced industrially by the oxidation/dehydrogenation of methyl alcohol (silver catalyst process) or by oxidation of methanol with air (Formox process). Both process depend on the use of catalysts, the first route using a silver catalyst, the second route employing a metal oxide catalyst. All formaldehyde produced from methyl alcohol is usually marketed in aqueous solution.

In 2000, European production of formaldehyde was 3.1 million tons; according to (IPPC Chemicals, 2002). This compares with a North American production capacity of 2 million tons and a Far eastern production capacity of 1.8 million tons. Global demand is expected to grow at roughly 2% per year in the mid-term. Major plants with capacities greater than 230'000 tons per year are located in France,

Germany, the Netherlands, Italy, Spain, Sweden, Austria, the US, Canada, and Japan, according to (Wells, 1999). According to (IPPC Chemicals, 2002), formaldehyde is used to produce:

- a large variety of resins generated through reaction with other compounds such as phenol or urea. These resins are used as adhesives, bonding agents, glues, paints, coating and other applications
- MDI (methyl diisocyanate), for polyurethanes
- Polyoxymethylene, a formaldehyde polymer used as an engineering plastic
- Polyols for water-soluble paints and coatings
- Hydraulic fluids and lubricants, etc.

39.5 System characterization

Formaldehyde can be produced by two routes, both involving the precursor methanol. One route involves oxidation and dehydrogenation in an aqueous solution (silver process), the other is carried out with oxygen (Formox process). In practice, both routes yield about 92%, but the Formox process is more economical.

39.5.1 Formaldehyde by the silver process

In the initial step, methanol is dehydrogenated (1). There is a secondary combustion of hydrogen (2), resulting in the overall reaction (3). The reaction takes place with air over a crystalline silver catalyst (IPPC Chemicals, 2002).



The reaction occurs at slightly elevated pressure and temperatures of 650 – 700 °C. Controlled amounts of water are fed into the reaction. Traces of methyl formate and formic acid are generated but their generation is minimized by rapid cooling. A 40-50% aqueous formaldehyde solution is obtained, concentrated and purified by distillation.

With total methanol conversion, steam is generated, as the steps (2) and (3) are exothermic. The reaction off-gas also contains about 18 – 23% hydrogen and can be incinerated with energy recovery, either in a boiler or for electricity and steam production.

The silver process can also be used for partial methanol conversion (about 80%). Only small amounts of water are used. The process solution contains excess methanol and is recycled. The off-gas from the process is combusted to generate steam. (IPPC Chemicals, 2002). In total and partial methanol conversion, steam is generated as a co-product (cf table 1.2).

39.5.2 Formaldehyde by the Formox process

Methanol is directly oxidized by air over a metal oxide catalyst at a temperature of 470 °C. excess heat is removed with an oil-transfer medium. The product gases are cooled, absorbed in water, and an aqueous 37% formaldehyde solution is obtained. (Wells, 1999) This process also produces steam as a co-product (see Tab. 39.2).



39.6 Life cycle Inventory for formaldehyde

The information in this part stems entirely from (IPPC Chemicals, 2002). The inventory is based on 100% formaldehyde production. The inputs and outputs are an average of the Silver and Formox processes.

Tab. 39.2 Processes and outputs associated with formaldehyde production

Inventory name	Description
Formaldehyde, production mix, at plant	Average of the Silver and formox processes
Oxidation of methanol	Multi-output process that produces 4854 and 4104
Steam from the production of formaldehyde	Steam that is exported from formaldehyde production

39.6.1 Precursor materials and fuels consumption

An overview of methanol and fuels consumption and of steam generated by these exothermic reactions is given in Tab. 39.3, taken from IPPC Chemicals (2002): Chapter 10.2.2. It is notable that 1.5 tons steam / ton formaldehyde are generated from off-gas combustion and heat from the exothermic reactions, thus forming „steam for export“.

Tab. 39.3 resource consumption and energy balance for formaldehyde production

	Silver process, total methanol conversion	Silver process, partial methanol conversion	Formox process
Methanol yield (%)	87-90	87-90	91-94
Methanol consumption (kg / ton 100% formaldehyde product)	1185 – 1226	1185 – 1226	1135 - 1170
Net steam export (ton / ton 100% formaldehyde product)	2.6*	0.4	2.0
Electricity consumption** (kWh / ton 100% formaldehyde)	100	100	200 - 225

* 45% stems from off-gas combustion

** includes off-gas combustion

According to an example given in IPPC Chemicals (2002): chapter 10.3.2, two thirds of the off-gases from a silver process are used for electricity generation, the rest being used for steam production. Since both the electricity and steam production efficiencies are about equal, it can be assumed that 1.3 MJ or 0.36 kWh of electricity stem from off-gas combustion, the remainder being grid electricity. This report assumes that an average of 150 kWh are required per tonne of product (100% formaldehyde).

Net steam export amounts to 1.5 – 2 ton / ton 100% formaldehyde product, according to Chapter 10.3.1 of IPPC Chemicals (2002). This is because both the silver and the Formox process are exothermic and in addition off-gases containing hydrogen stemming from the silver process can be incinerated. Based on a standard 37% formaldehyde product solution, there are approximately 0.5 – 0.7 tons of steam generated per ton of formaldehyde.

According to IPPC Chemicals (2002): Chapter 10.4.5.1, steam production (from a dedicated catalytic oxidizer) is charged at 6 Pounds per ton. This is a „conservative“ value. The mentioned IPPC report

indicates that a typical European plant producing 50 kt formaldehyde (37%) / year the cash costs of production ran to about 60 Pounds per ton of product, including a „small“ credit for steam production.

This indicates that 3 – 4 Pounds worth of steam are exported per 60 Pounds of formaldehyde. A typical mass x price split valuation of the products formaldehyde (37%) and steam indicates that approximately 6% of total environmental burdens can be allocated to exported steam. This allocation factor is not affected because this inventory relates to 100% formaldehyde, as accordingly more steam is produced.

39.6.2 Air emissions

Emissions from stacks and fugitives are given in the following table. Since both the silver and the Formox processes are prevalent, each process contributes half of each parameter connected to air pollution. Generally, the CEFIC values presented in (IPPC Chemicals, 2002) are given more credence.

Tab. 39.4 Air emission factors for formaldehyde (100%) production (g/kg)

Substance	Silver process	Formox process
NOx	0.3 – 0.45	none
CO	0.1 - 0.3	0.05 – 0.1
CO2	108*	Ng ***
dust	ng	0.005
Formaldehyde	ng	0.0004
Formaldehyde **	0.25	0.0006
VOC	ng	0.0016
VOC**	0.0006 – 0.003	0.003
Methanol**	0.31	0.0007
Dioxins, related compounds***	ng	ng

* thermal incineration

** storage vents and fugitives

*** is taken from the silver process

39.6.3 Wastewater emissions (IPPC Chemicals, 2002)

Under routine operating conditions, both the silver and the formox processes do not emit any significant amounts of wastewater. Effluents may stem from spills etc. A Formox plant is reported to have an effluent stream of 0.008 g/kg COD (post-treatment value). This value is taken for both processes.

39.6.4 Liquid wastes (IPPC Chemicals, 2002)

None given.

39.6.5 Solid wastes (IPPC Chemicals, 2002)

The main solid wastes are spent catalysts. These are usually sent to a reclaimer for recovery of the valuable metals (silver, iron and molybdenum). The inert catalyst carrier is disposed of by the reclaimer, probably to landfill.

A small build-up of paraformaldehyde may occur and is routinely removed during maintenance. According to (IPPC Chemicals, 2002) the paraformaldehyde is either redissolved and fed back into the production line or incinerated.

Tab. 39.5 Solid waste from formaldehyde plants (g/kg)

Substance	Silver process	Formox process
Process catalyst	0.04 – 0.1	0.01 – 0.06
Off-gas incinerator catalyst	0.002 – 0.015	ng
Oil filters, sewer sludge	0.06*	0.51

sludge not included

Note: the solid wastes are not included in the inventory.

39.6.6 Infrastructure and Transport

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.0000000004 units per kg of produced formaldehyde.

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007b) are used for the different raw materials.

39.7 Data quality considerations

The data quality is considered to be good, as the values taken from literature stem from actual measured values. The fuels input data are in part an approximation, although the energy usage is monitored, as are the amounts of precursor substances.

The following table summarizes the input and output data as well as the uncertainties used for the production of formaldehyde from both the silver and the Formox processes. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 39.10.

Tab. 39.6 Input / output data and data quality for formaldehyde production in Europe

Explanations	Name	Location	Unit	oxidation of methanol	Uncertainty Type	Standard Deviation 95%	General Comment	formaldehyde, production mix, at plant	steam from the production of formaldehyde
	Location		RER					RER	RER
	Infrastructure Process Unit		0					No kg	No kg
Input from Technosphere	chemical plant, organics disposal, catalyst base CH ₂ O production, 0% water, to residual material landfill electricity, medium voltage, production UCTE, at grid	RER CH	unit kg	4.00E-10 5.00E-02	1 1	1.22 1.56	(2,2,1,2,1,5); infrastructure of a typical plant (4,2,1,2,1,5); disposal of catalyst base material	94 94	6 6
	methanol, at plant	UCTE	kWh	1.50E-01	1	1.22	(2,2,1,2,1,5); electricity	94	6
	transport, freight, rail	GLO	kg	1.20E+00	1	1.22	(2,2,1,2,1,5); precursor	94	6
	transport, lorry 32t	RER	tkm	7.20E-01	1	1.22	(2,2,1,2,1,5); transport	94	6
water emission	BOD ₅ , Biological Oxygen Demand COD, Chemical Oxygen Demand	RER	tkm	1.20E-01	1	1.22	(2,2,1,2,1,5); transport	94	6
air emission	Heat, waste	-	kg	8.00E-06	1	1.22	(2,2,1,2,1,5); wastewater	94	6
	Carbon dioxide, fossil	-	kg	8.00E-06	1	1.22	(2,2,1,2,1,5); wastewater	94	6
	Carbon monoxide, fossil	-	MJ	5.40E-01	1	1.22	(2,2,1,2,1,5); waste heat	94	6
	Formaldehyde	-	kg	1.00E-04	1	1.22	(2,2,1,2,1,5); emissions	94	6
	Methanol	-	kg	2.50E-05	1	1.22	(2,2,1,2,1,5); emissions	94	6
	Nitrogen oxides	-	kg	3.10E-05	1	1.22	(2,2,1,2,1,5); emissions	94	6
	NMVO _C , non-methane volatile organic compounds, unspecified origin	-	kg	3.80E-04	1	1.22	(2,2,1,2,1,5); emissions	94	6
	Particulates, > 2.5 um, and < 10um	-	kg	3.00E-06	1	1.22	(2,2,1,2,1,5); emissions	94	6
Outputs	formaldehyde, production mix, at plant	RER	kg	5.00E-06	1	1.22	(2,2,1,2,1,5); emissions	100	0
	steam from the production of formaldehyde	RER	kg	2.3				0	100

39.8 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

39.9 Conclusions

The inventory for formaldehyde is based on literature, representing the actual production situation in Europe. The dataset is in accordance with the present quality guidelines of the ecoinvent project. The data are thus of a quite good quality and can be used in a broad context.

39.10 EcoSpold Meta Information

ReferenceFunction	Name	oxidation of methanol
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	cradle-to-gate, including all precursors, ancillary materials and transports
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Oxidation von Methanol
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The processes that are used to produce formaldehyde from methanol are described in this inventory. These processes also produce steam, which carries part of the total environmental burdens. The process "oxidation of methanol" is a multi-output process
ReferenceFunction	CASNumber	
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	RER
Technology	Text	represents a current cross-section of actual plants in Europe
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	see technology
Representativeness	UncertaintyAdjustments	none

39.11 References

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40 Helium

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 Last changes:

10.12.2007

40.1 Introduction

Helium is a light, non-flammable and chemically inert gas. Although it is one of the most abundant elements in the universe, most of it exists outside the earth's atmosphere.

Terrestrial helium is generated underground by the radioactive decay of uranium, thorium and other heavy elements. Some of this helium becomes trapped under impermeable layers of rock and mixes with the natural gas formed there. If the helium finds its way to the surface, it quickly rises in the atmosphere and escapes into space. The amount of helium found in various natural gas deposits varies from almost zero to as much as 4 percent by volume. Natural gas sources with the highest concentrations of helium are found in the United States.

40.2 Characterisation of material product

Helium has the lowest boiling point of all the elements and does not solidify at atmospheric pressure and 0 K. It is the second lightest element (after hydrogen) and has the smallest molecular size of all the elements. Moreover, it is chemically inert and has a very high specific heat capacity and high thermal conductivity. These properties make it ideal for a wide variety of industrial, commercial and research applications. Tab. 40.1 shows the physical properties of helium.

Tab. 40.1 Physical properties of helium

Property	Unit	Value
Molecular weight	g mol ⁻¹	4.00
Specific gravity, gas ¹	kg Nm ⁻³	0.1785
Normal boiling point	K	4.3
Specific gravity, liquid ²	kg m ⁻³	124.98
Specific heat capacity c _p ¹	kJ kg ⁻¹ K ⁻¹	5.24
Specific heat capacity c _v ¹	k J kg ⁻¹ K ⁻¹	3.16
Heat of vaporisation ²	kJ kg ⁻¹	22.28

¹ At 273.15 K and 0.1013 MPa (Cerbe & Hoffmann, 1990)

² At normal boiling point (Flynn, 2005)

40.3 Reserves and resources of the material

At present, helium-bearing natural gases are the only source from which helium can be extracted economically. All the major gas projects of recent years (Qatar, Algeria, Papua New Guinea, Australia etc.) have included the extraction of helium where its concentration in the gas exceeds 0.1 percent (TNK-BP, 2006). The economics of helium extraction are driven by natural gas recovery and sale as well as by the separation of natural gas liquids (NGL) and its value as a by-product (sold or vented).

Most natural gas fields with an average helium content of up to 0.3 percent are found in the United States. Outside America, helium is found in Algeria, Poland, Russia, Quatar and a few small reserves in other areas. The largest reserves with a helium content ranging between 0.1 and 0.3 percent are found in the Middle East (Lemak, 2001). According to Pacheco (2006), worldwide helium reserves amount to $39.7 \cdot 10^9$ Nm³. A quarter of these are found in Quatar, 21 percent in Algeria and the United States, 17 percent in Russia and 16 percent in other countries.

World helium production in 2005 is estimated to be $160 \times 10^6 \text{ Nm}^3$ (Pacheco, 2006). The largest producer and consumer of helium is the United States, with a consumption of more than 50 percent of world production. It is followed in second place by the European Union with a consumption of 20 percent of world production and in third place by the Asia Pacific region with 15 percent (TNK-BP, 2006).

The European helium consumption of about $30 \times 10^6 \text{ Nm}^3$ is produced mainly by plants in Poland (O-dolanów), Russia (Orenburg), and Algeria (Arzew, Bethouia, Skikda) or is imported from the United States (Bräutigam & Clausen, 2003). According to the EC (2006), 32 percent of the helium consumed within Europe in 2005 was imported from the United States.

Russia extracts 5 to $6 \times 10^6 \text{ Nm}^3$ of helium per year and consumes about $1 \times 10^6 \text{ Nm}^3$. The rest is liquefied and sold, mainly to Europe (PGNiG, 2006). In 1995, a plant was constructed in Algeria producing $15 \times 10^6 \text{ Nm}^3$ of liquid helium per year and in 2005 another plant was commissioned in Qatar producing 6 to $7 \times 10^6 \text{ Nm}^3$ per year. In 2006, Algeria launched its second plant with a production output of 6 to $7 \times 10^6 \text{ Nm}^3$ per year (TNK-BP, 2006). In Poland, $3 \times 10^6 \text{ Nm}^3$ of helium per year were produced in 2004 (Pacheco, 2006).

Helium can also be produced by liquefying air and separating the component gases. It is present in dry air at a concentration of only 0.0005%. The production costs for this method are consequently high, and it is rarely used to produce the gas.

40.4 Use / application of product

Helium is known as a non-flammable substitute for hydrogen in providing the lift for blimps and balloons. Thanks to its inertness, gaseous helium is used as a welding gas, a shield gas and a carrier gas. Because of the small molecular size of helium, it is used for leak detection. Other applications of helium are optical fibre manufacture, the semiconductor industry and for purging rocket engines (EC, 2006). Fig. 40.1 shows the share of worldwide demand for helium (gaseous and liquid) in 2002 (Smith et al., 2005).

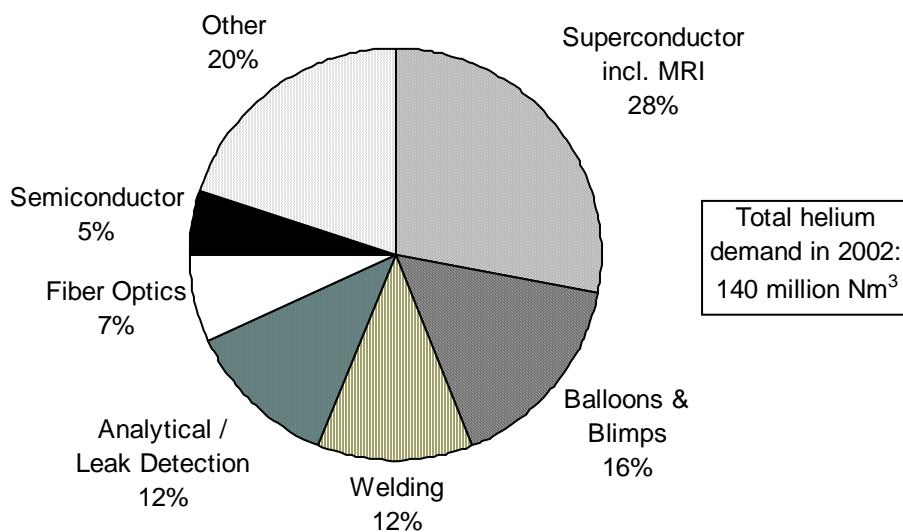


Fig. 40.1 Share of worldwide demand for helium in 2002 (Source: Smith et al., 2005)

40.5 System characterisation

Helium is a by-product of the production of natural gas and liquid natural gas (LNG). While sources in the United States, Poland and Russia are connected to natural-gas production facilities, the newer helium sources in Algeria and Qatar typically extract the gas within the process of producing LNG (EC, 2006).

Helium is typically separated from helium-bearing natural gas by a low-temperature liquefaction process (-180 °C) that removes the crude helium as a gas from the liquefied portion, which consists mainly of hydrocarbons. Crude helium contains 65 to 80 percent helium and 20 to 35 percent nitrogen. The still gaseous crude helium is sent to a helium refining plant for further purification. Crude helium is typically purified at ambient temperature using pressure swing adsorption (PSA) to grade A helium with a purity of 99.995 % or higher.

Because helium is stored and transported in liquid form to the cylinder-filling centres in order to be transformed into compressed gas, the refined helium is piped into the liquefier, where it is liquefied at a temperature of -269°C.

The resulting liquid helium is typically shipped to the cylinder-filling centres in sealed 40000-litre multi-layered vacuum-insulated liquid containers shielded with liquid nitrogen. Around 0.3 percent of the liquid helium evaporates per day during transportation. The evaporated helium increases the pressure in the tank, but it does not leak because of the hermetically sealed tank construction (Bräutigam & Clausen, 2003).

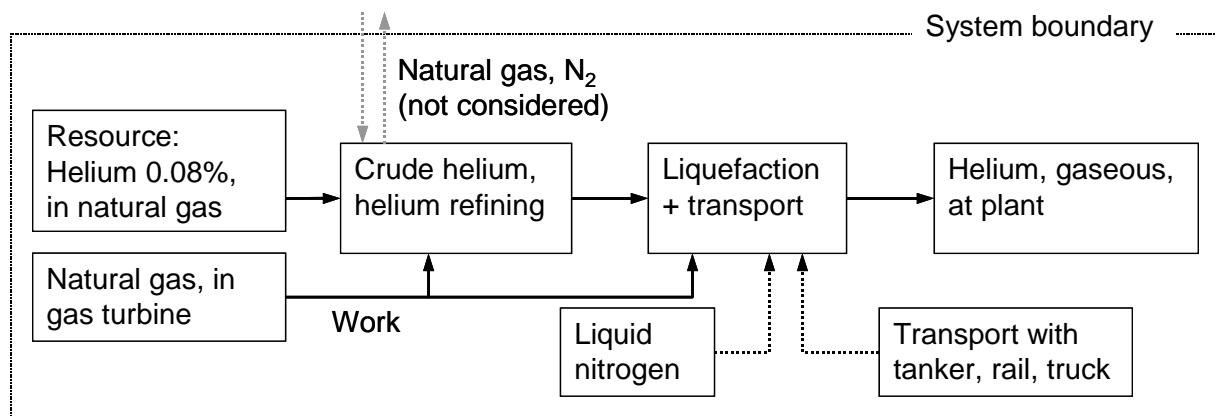


Fig. 40.2 System outline for the production of helium, gaseous, at plant

40.6 Helium, gaseous, at plant

40.6.1 Process

Because crude helium is a by-product of natural gas production when higher hydrocarbons or nitrogen are removed from the natural gas during the refining process, only a part of the energy needed for this process is accounted to the helium production. If no helium is extracted, the hydrocarbon-nitrogen-helium mixture⁷ is vented or used as fuel. In order to raise the helium concentration, the gas is further cooled and the hydrocarbons and nitrogen are separated until raw helium with a concentration of 65 to 80 percent helium and 20 to 35 percent nitrogen is obtained. Only this second process step is accounted to the helium production.

⁷ Typical composition: 55 Mol-% N₂, 40 Mol-% CH₄, 5 Mol-% He

No detailed information is available about the helium refining process with pressure swing adsorption. Because this process is carried out at ambient temperature and moderate pressure (15-20 bar), the energy requirement for this process step is neglected. According to Häussinger et al. (2005), this refining process has a yield of practically 100%, therefore no helium losses are included in the calculation.

Considerable energy is needed to liquefy the refined helium by cooling it down to -269°C in order to ship it to the cylinder-filling centres where it is filled as gas into pressurised steel cylinder or tube trailers.

40.6.2 Energy use and auxiliaries

Production of raw helium

An energy requirement of 0.83 MJ/kg is given by Norwood et al. for the production of raw helium containing 67 volume percent of helium (2004). Due to the high specific weight of nitrogen, an energy requirement of 3.7 MJ/kg of helium is calculated from this figure assuming that the remaining 33 percent is only nitrogen.

A similar energy requirement is calculated for the cooling process used to separate most of the nitrogen and hydrocarbons from the flue gas obtained from the natural-gas refining step (to produce raw helium with 70 volume percent helium). An energy requirement of 3 MJ/kg helium is calculated assuming a 50% process efficiency of a Carnot process for cooling from -160°C to -196°C and a 36 percent efficiency for the gas turbine used for supplying the energy needed for the cooling process. An energy requirement of 3 MJ per kg helium is used here: it is provided by the process “natural gas, burned in a gas turbine”.

Liquefaction of refined helium

A small liquefaction plant with a production capacity of 20 litres of liquid helium per hour needs an (electrical) power input of 90 kW (Kühlwein, 2003). This leads to a specific power demand of 36 kWh per kg of helium. A Stirling refrigeration process with a production capacity of 10 litres of liquid helium per hour needs 2.8 kWh (electricity) per litre of liquid helium (22 kWh/kg helium). A very large liquefier used for superconducting magnets with a production capacity of 3,000 litres of liquid helium per hour needs a power input of 2900 kW (7.7 kWh/kg helium) for the liquefaction process (Häussinger et al., 2005).

A medium-sized liquefaction plant with annual production of $10 \times 10^6 \text{ Nm}^3$ of helium (equal to 1,800 tons per year or about 1,800 litres of liquid helium per hour) is used. According to Flynn (2005), a plant of this size has an efficiency of about 20 to 50 percent of a Carnot process. For such a plant, a power requirement of about 13 kWh/kg of helium for the liquefaction process is calculated assuming an efficiency of 40 percent of a Carnot process. The plant efficiency is primarily a factor of its size. It is higher for very large plants (Flynn, 2005), which explains the lower specific power consumption of the large 3000 litre/h plant described by Häussinger et al. (2005).

A value of 13 kWh/kg helium is used here. It is assumed that this power is produced by a gas turbine with an efficiency of 36 percent. This leads to an energy requirement (as natural gas) of 130 MJ per kg of helium provided by the process “natural gas, burned in a gas turbine”.

Liquid nitrogen for cooling transport tanks

During the transport of liquid helium, 32 kg of liquid nitrogen is used per day for shielding a liquid helium tank of 40000 litres volume or 5,000 kg of helium (Kirk-Othmer, 1995). According to the EC (2000), the average transport time (one way) for delivery from the United States is 20 days, from Algeria 8 days and from Eastern Europe 9 days (see Tab. 40.2). An average transport time of 12 days is

used here, which leads to a liquid nitrogen consumption during transport of 0.077 kg N₂ per kg of helium.

40.6.3 Emissions

Emissions to air are included in the unit processes used (e.g. natural gas in a gas turbine). No further process-related emissions are included. The nitrogen (N₂) emitted from the refining process and from the vented nitrogen during transport is not accounted. Due to the high process yield of practically 100% within the refining process, no helium emissions are accounted. During transport of the liquid helium, part of the helium evaporates but is captured within the sealed tank. Helium losses occurring during transport are consequently not included in the calculation either.

40.6.4 Transportation to cylinder-filling centre

The average transport distance is calculated according to the helium consumption in Europe and the estimated production shares for Europe based on Pacheco (2006) and the EC (2006) (see Tab. 40.2). Due to the great weight of the liquid helium tanks (estimated as 0.25 kg per litre), and the low weight of liquid helium (0.125 kg per litre), the amount of transport needed is multiplied by a factor of three.

Tab. 40.2 Average transportation needed for European helium supply, per kg helium to helium cylinder-filling centre

Property	Amount ¹	Distance	Transport time	Tanker transport ²		Rail transport ²		Road transport ²	
				km	tkm	km	tkm	km	tkm
Imported from	t / year	km	Days	km	tkm	km	tkm	km	tkm
United States	1730	12000	20	10000	30.0	1000	3.0	1000	3.0
Algeria	2230	1000	8	1000	3.0	0	0	0	0
Poland	540	700	4	0	0	600	1.8	100	0.3
Russia	900	3000	9	0	0	3000	9.0	0	0
Average	5400	4800	12	3600	10.8	867	2.6	333	1.0

¹ Estimate for the supply mix of helium consumed in Europe based on Pacheco (2006) and the EC (2006) and a European consumption of $30 \cdot 10^6$ Nm³ (5,355 t).

² Amount of transport services needed is multiplied by a factor of three due to the great weight of tank insulation.
Type of transport estimated.

40.6.5 Infrastructure

No specific data are available for the infrastructure of helium production. The size of the infrastructure is approximated with reference to a production facility for air separation with a plant weight of 100 tons. According to the EC (2000) and Flynn (2005), a plant producing 1,800 tons of helium per year costs about $\$60-130 \cdot 10^6$ and has an estimated weight of 1,000 tons. With an assumed plant service life of 20 years, the infrastructure requirement of the proxy process used is $2.8 \cdot 10^{-7}$ units per kg of helium. The infrastructure of the storage or transport tanks is neglected. The infrastructure required for transport is included in the transport processes.

40.6.6 Data quality considerations

Tab. 40.3 shows the unit process raw data and data-quality indicators of the inventory of helium, gaseous, at plant.

A simplified approach with a pedigree matrix is used to calculate the standard deviation. However, the basic uncertainty has been adjusted to represent the ranges of the data obtained from a study of the literature. The inventory is based only on a few sources for the amount of energy and process materials. Large uncertainties exist for the transport distances and the infrastructure. This inventory should not be used for gaseous helium delivered directly from the refining plant without liquefying for transport.

Tab. 40.3 Unit process raw data of helium, gaseous, at plant

product	Name Location InfrastructureProcess Unit	Location InfrastructureProcess Unit	UncertaintyType		StandardDeviation 95%	GeneralComment
			RER 0 kg	helium, gaseous, at plant		
technosphere	helium, gaseous, at plant	RER 0 kg	1			
	natural gas, burned in gas turbine	GLO 0 MJ	1.33E+2	1	1.56	(3,4,2,2,4,4); energy demand estimated from various literature data
	nitrogen, liquid, at plant	RER 0 kg	7.70E-2	1	1.33	(2,4,4,2,1,5); estimation based on one source and transport duration
	transport, lorry >16t, fleet average	RER 0 tkm	1.00E+0	1	2.14	(4,2,2,2,3,5); estimation according to origin of helium and tank weight
	transport, freight, rail	RER 0 tkm	2.60E+0	1	2.14	(4,2,2,2,3,5); estimation according to origin of helium and tank weight
	transport, transoceanic freight ship	OCE 0 tkm	1.08E+1	1	2.14	(4,2,2,2,3,5); estimation according to origin of helium and tank weight
resource, in ground	air separation plant	RER 1 unit	2.80E-7	1	3.36	(4,5,2,2,4,5); rough estimation for infrastructure demand
	Helium, 0.08% in natural gas, in ground	- - kg	1.00E+0	1	1.07	(2,nA,nA,nA,nA,nA); input

40.7 Cumulative results and interpretation

40.7.1 Introduction

Selected LCI results and values for the cumulative energy requirement are presented and discussed in this section. Please note that only a small part of the 1500 elementary flows is presented here. The selection of the elementary flows shown in the tables is not based on their environmental relevance. Rather, it allows the contributions of the different life cycle phases or specific inputs from the technosphere to the selected elementary flows to be illustrated. Please refer to the *ecoinvent* database for the complete LCIs.

The selection shown is unsuitable for a life-cycle assessment of the analysed processes and products. Please download data from the database for your own calculations, not least because of possible minor deviations between the presented results and the database due to corrections and changes made in the background data used as inputs to the relevant dataset.

The *ecoinvent* database also contains the results of life-cycle impact assessments. Assumptions and interpretations are necessary to match current LCIA methods to the *ecoinvent* inventory results. They are described in Frischknecht et al. (2007). You are strongly advised to read the respective sections of the implementation report before applying the LCIA results.

40.7.2 Selected LCI results

The major part of the carbon dioxide (94%), NMVOC (87%), nitrogen oxide emissions (85%) and the cumulative energy demand (fossil: 95%) are caused by the liquefaction process. The transport from the production site to the cylinder-filling centres is with 3-13% of lower importance for the carbon dioxide, NMVOC, nitrogen oxide emissions and the cumulative energy demand (fossil). The production infrastructure is for the land use (49%), the cadmium (78%) and particulate emissions (39% of PM <2.5um) the most important impact. Tab. 40.4 shows selected LCI results and cumulative energy demands for the process helium, gaseous, at plant.

Tab. 40.4 Selected LCI results and the cumulative energy demand for helium, gaseous, at plant

Ecocat	Ecosubcat	Name	Name	helium, gaseous, at plant
			Location Unit	RER kg
cumulative energy demand	fossil	non-renewable energy resources, fossil	MJ-Eq	1.65E+02
	nuclear	non-renewable energy resources, nuclear	MJ-Eq	2.30E+00
	primary forest	non-renewable energy resources, primary forest	MJ-Eq	1.13E-04
	water	renewable energy resources, water	MJ-Eq	5.86E-01
	biomass	renewable energy resources, biomass	MJ-Eq	9.93E-02
	wind	renewable energy resources, kinetic (in wind), converted	MJ-Eq	4.03E-02
	geothermal	renewable energy resources, geothermal, converted	MJ-Eq	0.00E+00
	solar	renewable energy resources, solar, converted	MJ-Eq	5.61E-04
selected LCI results	resource	land occupation	m2a	2.95E-02
	air	CO2, fossil	kg	8.92E+00
	air	NM VOC	kg	3.62E-03
	air	nitrogen oxides	kg	2.37E-02
	air	sulphur dioxide	kg	5.79E-03
	air	particulates, <2.5 um	kg	3.53E-04
	water	BOD	kg	1.97E-03
	soil	cadmium	kg	1.43E-09

40.8 Conclusions

The production of helium is determined largely by the impact of liquefaction process. Liquefaction is needed because helium is stored and transported in liquid form to the cylinder-filling centres. A large part of the helium consumed in Europe is imported in liquid form from plants in Poland, Russia, Algeria and the United States. Due to the large impact of liquefaction process this process is not suitable for helium used directly from the production plant (no liquefaction needed). Also not considered is the recovery of helium from processes which use large amounts of helium.

40.9 Appendices: EcoSpold Meta Information

Tab. 40.5 EcoSpold Meta Information of helium, gaseous, at plant

ReferenceFunction	Name	helium, gaseous, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
DataSetInformation	Type	1
	Version	2.0
	energyValues	0
	LanguageCode	en
	LocalLanguageCode	de
DataEntryBy	Person	72
	QualityNetwork	1
ReferenceFunction	DataSetRelatesToProduct	1
	IncludedProcesses	The module includes the most important energy demand and resources used for production, the transport to a cylinder filling centres and an estimation for infrastructure.
	Amount	1
	LocalName	Helium, gasförmig, ab Werk
	Synonyms	
	GeneralComment	The module reflects the production of helium from natural gas. The processed natural gas input and output is not included in the inventory. Further included is the liquefaction of the product gas and the transport to a cylinder filling centre within Europe, where the gas is evaporated and compressed into cylinders.
	InfrastructureIncluded	1
	Category	chemicals
	SubCategory	inorganics
	LocalCategory	Chemikalien
	LocalSubCategory	Anorganika
	Formula	He
	StatisticalClassification	
	CASNumber	007440-59-7
TimePeriod	StartDate	2000
	EndDate	2005
	DataValidForEntirePeriod	1
	OtherPeriodText	
Geography	Text	Transport processes represent helium demand in central Europe. Production from Algeria, United States, Russia and Poland.
Technology	Text	Helium extraction from natural gas. Refining to grade A helium with pressure swing adsorption (PSA). Liquefaction and transport to cylinder filling centres within Europe. Natural gas used for compression work in cooling processes.
Representativeness	Percent	
	ProductionVolume	25200 t
	SamplingProcedure	based on literature
	Extrapolations	none
	UncertaintyAdjustments	none
DataGeneratorAnd	Person	72
	DataPublishedIn	2
	ReferenceToPublishedSource	8
	Copyright	1
	AccessRestrictedTo	0
	CompanyCode	
	CountryCode	
	PageNumbers	helium
ProofReading	Validator	42
	Details	automatic validation in Excel
	OtherDetails	none

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41 Hydrochloric acid

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41.1 Introduction

This chapter describes the production of hydrogen chloride (HCl). In Western Europe, hydrogen chloride is for the most part a by-product of product chains and is recycled into captive uses (e.g. ethylene dichloride, EDC). (Euro Chlor, 1997)

Synonyms for hydrochloric acid: Hydrogen chloride, Muriatic Acid

41.2 Reserves and resources of hydrogen chloride

Hydrogen chloride is an inorganic compound. It is for the most part produced as a by-product of product chains described below.

41.3 Characterisation of hydrogen chloride

Hydrogen chloride (HCl, CAS-No. 7647-01-0) is a colorless to yellowish fuming liquid with a sharp, pungent odor. It is a strong highly corrosive acid. HCl is soluble in water and alcohol but is not soluble in hydrocarbons..HCl has a molecular weight of 36.45 and boils at 85°C. (Inchem hcl)

Hydrochloric acid is marketed under different technical grades: Technical Grade HCl (31%-33%), C.P. Grade (36%-38%) (Inchem hcl)

HCl concentration is frequently given as ° Baume. 20 ° Baume corresponds to between 31.45 – 33.3 wt % HCl in an aqueous solution.

41.4 Production and use of HCl

In Western Europe, the recycling of HCl is a major source of chlorine supply. The main source of HCl is ethylene dichloride (EDC), which also the major user (see chapter on EDC). Another main and growing source of HCl is from the phosgene chain, which is a precursor for polyurethanes. Other non-chlorine containing products which contribute to HCl supply are HFC's such as Teflon. HCl from CHC waste incineration is not a major source. Synthetic HCl is produced in only small quantities.

Tab. 41.1 1995 values for HCl supply in Western Europe (Euro Chlor 1997)

Material / Process	Supply (Mio tons)
EDC – Vinyl chloride	3.07
Phosgene – polyurethane chain	0.8
HCl synthesis *	0.22
CHC incineration	0.19
Sodium sulfate	0.27
Others (including chlor-alkali production etc.) **	1.15
Total	5.7

* combustion of chlorine

** a significant contributor is HFC production (no figures available). Others include perchloroethylene, dichloromethane, trichloroethylene.

Tab. 41.2 1995 values for HCl demand in Western Europe (Euro Chlor 1997)

Material / Process	Demand (Mio tons)
EDC	3.135
Net sales	0.9
internal use such as pH neutralisation	0.6
Others (including chlor-alkali production ***, methyl chloride, etc.)	1.0
Total	5.7

*** The chlor-alkali production not only generates HCl but also is a user

Tab. 41.1 and Tab. 41.2 indicate that most of the produced HCl directly enters into other processes, and that relatively little is actually sold on the market (net sales in 1995 amounted to only 15% of the total demand). For the sake of simplicity, this report will assume that HCl originating from the EDC/VCM process is captive, i.e. resembles a closed-loop system. It is not sold on the open market.

Total US annual HCl production was 4.2 million tons in 1997, according to (EPA HCl 2003). Most of the production is captive and goes into designated uses Only about 5% of the HCl produced in the US is from direct production (i.e. not as a by-product). In Europe in 1995, this figure was roughly 4% (see table 1.1).

Producers include BASF, Dow, DuPont and many small- and midsize companies. The main applications for HCl are according to (Inchem hcl):

- Acidizing (activation) of petroleum wells
- Manufacture of dyes, phenols and plastics
- Ore reduction (manganese, radium, vanadium, tantalum, tin and tungsten)
- Food processing (corn, syrup, sodium glutamate)
- Pickling and metal cleaning
- Industrial acidizing
- Water treatment
- Resin regeneration and demineralizers

41.5 System characterization

As described above, HCl can be either directly prepared or generated as a by-product from a number of reactions. These HCl production pathways are summarily described below.

41.5.1 HCl synthesis

The process involves burning hydrogen gas and chlorine gas combustion chamber, producing hydrogen chloride gas. The hydrogen chloride gas then passes through a cooler to an absorber where process water s introduced, producing aqueous hydrochloric acid. (Inchem hcl)



41.5.2 HCl as a by-product of the phosgene – polyurethane chain

The phosgene-polyurethane chain, according to (Eurochlor 1997), is a significant and growing contributor to the HCl supply. A closer look at the chain shows that phosgene is transformed to the two intermediaries toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Both TDI and MDI production results in hydrogen chloride gas, which can be either sold in gas form via pipeline or in solution.

The APME reports for MDI and TDI, the basis for the Ecoinvent inventories - do not contain any data on HCl production. UBA 55/91 however indicates that a total of 2 kg of HCl are generated per kg of MDI and that a total of 3.22 kg of HCl are generated per kg of TDI

Assuming the HCl produced by the MDI and TDI processes is sold, the mass x price ratio of HCl to MDI or TDI can determine whether or not an allocation to HCl can be made.

Tab. 41.3 1999/2000 prices for HCl, TDI, MDI (Chemical Profiles)

Material / Process	\$ / tonne (2200lbs)	Mass x price ratio (HCl : MDI or TDI) based on production fig- ures in (UBA 55/91)
HCl	79.2 (22 deg. Baume, US Gulf, tanks, works)	-
MDI	3'100	5%
TDI	2'100	12%

The figures in Tab. 41.3 indicate that HCl from the phosgene-polyurethane chain, should it be sold on the market, does carry environmental burdens stemming from the production of MDI or TDI. However, due to a lack of data in the corresponding reports in Hischier (2003), at present no allocation can be made.

41.5.3 HCl as a by-product of fluorochlorocarbon production

The production of polytetrafluoroethylene (PTFE) and its precursor compounds trichloromethane and chlorodifluoromethane also produces the by-product HCl (see chapter 65 of this report here). The following chemical reactions are used to create those monomers:



- (1) production of hydrogen fluoride.
- (2) production of trichloromethane. The by-product HCl (0.92kg/kg) is not considered in the mentioned chapter on PTFE production.
- (3) production of chlorodifluoromethane. The ratios in selling price of the two products are: HCl : chlorodifluoromethane = 2.8 : 97.2. The by-products HCl (0.367kg/kg) and trifluoromethane are not considered in the mentioned chapter on PTFE production.

- (4) production of PTFE. The ratios in selling prices of the two products are: HCl : PTFE = 0.5 : 99.5. The by-product HCl (0.18kg/kg) is not considered in the mentioned chapter on PTFE production.

41.5.4 HCl as a by-product in perchloroethylene, dichloromethane, trichloroethylene production

No allocation to HCl is made in the respective chapter of this report here (see chapter 24).

Tetrachloroethylene (PER) and trichloroethylene (TRI) are co-produced by oxychlorination of ethylene dichloride. Minimal amounts of aqueous hydrogen chloride are obtained (Wells, 1999). Oxychlorination or chlorinolysis of raw materials such as propylene, 1,2-dichloroethane, chloropropenes and chloropropanes also co-produces PER with trichloroethylene by the so-called "TRI/PER" process:



The production of methylene dichloride takes place by methane chlorination. This production process can be described with the following equations:



41.5.5 1.5.5 HCl from sodium sulfate production

An allocation to HCl is made in the sodium sulphate production (see chapter 75 of this report), based on the so-called Mannheim production process:



41.6 Life cycle Inventory for HCl

This report assumes that HCl is generated from combustion of chlorine with hydrogen as well as from the sodium sulfate pathway. As both routes produce nearly equal amounts of HCl (see table 1.1), it is assumed that they each amount to 50% of HCl production that is actually sold on the market. In fact, they each amount to only 25% of the total HCl sales, but due to a lack of data for the other processes (see above), these amounts are assumed to generate total sales volume. The inventory for HCl from sodium sulfate production is described in chapter 75.

41.6.1 Precursors (direct HCl production)

Tab. 41.4 precursors per kg 100% HCl (estimated from molar weights)

Input	kg
Hydrogen	0.027
Chlorine	0.973

41.6.2 Energy consumption (direct HCl production)

The reaction of chlorine with hydrogen is highly exothermic. The heat of reaction may be sufficient to run the production. For this reason, it is assumed that no thermal energy is required for this reaction. A value for the electrical energy is not given but is assumed to be 1.2 MJ / kg product, based on a large chemical plant site in Germany producing 2.05 Mt per year (intermediates included) of different chemicals (Gendorf 2000):

41.6.3 Air emissions (direct HCl production)

No information available, however, this report assumes that 0.2 % of the chlorine input is emitted (1.9 g).

41.6.4 Wastewater emissions (direct HCl production)

no information available

41.6.5 Liquid wastes (direct HCl production)

no information available

41.6.6 Solid wastes (direct HCl production)

no information available

41.6.7 Transports and infrastructure

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.000000004 units per kg of produced hydrochloric acid (HCl).

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

41.7 Data quality considerations

The data quality is considered to be poor, as HCl by-product formation from sodium sulfate is estimated and HCl from TDI, MDI and other processes could not be accounted for, due to a lack of data.

The following tables summarize the input and output data as well as the uncertainties used for the direct production of hydrogen chloride as well as for the production mix (direct production & HCl aus Mannheim process). Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 41.10.

Tab. 41.5 Input / output data and data quality for hydrochloric acid (direct HCl production)

	Name	Location	Unit	hydrochloric acid, from the reaction of hydrogen with chlorine, at plant	Uncertainty Type	Standard Deviation 95%	General Comment
	Location			RER			
	Infrastructure Process			0			
	Unit			kg			
Input from Technosphere	chemical plant, organics	RER	unit	4.00E-10	1	1.32	(4,5,1,1,1,4); infrastructure
	chlorine, liquid, production mix, at plant	RER	kg	9.73E-01	1	1.26	(3,5,1,1,1,4); precursor
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.30E-01	1	1.16	(3,3,1,1,1,4); power
	hydrogen, liquid, at plant	RER	kg	2.70E-02	1	1.26	(3,5,1,1,1,4); precursor
	transport, freight, rail	RER	tkm	1.00E-01	1	1.24	(4,3,1,1,1,4); transport
	transport, lorry 32t	RER	tkm	5.00E-02	1	1.24	(4,3,1,1,1,4); transport
air emission	Chlorine	-	kg	1.90E-03	1	1.24	(4,3,1,1,1,4); emissions to air
	Heat, waste	-	MJ	1.20E+00	1	1.12	(1,3,1,1,1,4); waste heat
Outputs	hydrochloric acid, from the reaction of hydrogen with chlorine, at plant	RER	kg	1			

Tab. 41.6 Input / output data and data quality for production mix of hydrochloric acid

	Name	Location	Unit	hydrochloric acid, 30% in H ₂ O, at plant	Standard Deviation 95%	General Comment
	Location			RER		
	Infrastructure Process			0		
	Unit			kg		
Input from Technosphere	hydrochloric acid, from the reaction of hydrogen with chlorine, at plant	RER	kg	0.5	1.16	(3,3,1,1,1,4); Product
	hydrochloric acid, from Mannheim process, at plant	RER	kg	0.5	1.16	(3,3,1,1,1,4); Product
Outputs	hydrochloric acid, 30% in H ₂ O, at plant	RER	kg	1		

41.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

41.9 Conclusions

The inventories for hydrochloric acid are based on literature, theoretical reflections, estimations and assumptions. These unit process raw data are meant to be used as background information if HCl is used for a product in small amounts. Therefore these data can only give a rough approximation. They are not reliable enough for direct comparison of the various production ways or of this material with other, alternative products.

41.10 EcoSpold Meta Information

ReferenceFunction	Name	hydrochloric acid, from the reaction of hydrogen with chlorine, at plant	hydrochloric acid, 30% in H ₂ O, at plant
Geography	Location	RER	RER
ReferenceFunction	InfrastructureProcess	0	0
ReferenceFunction	Unit	kg	kg
ReferenceFunction	IncludedProcesses	Precursor compounds, auxiliary materials, transports, infrastructure.	Precursor compounds, auxiliary materials, transports, infrastructure.
ReferenceFunction	Amount	1	1
ReferenceFunction	LocalName	Chlorwasserstoff, aus der Reaktion von Chlor mit Wasserstoff, ab Werk	Chlorwasserstoff, 30%in H ₂ O, ab Werk
ReferenceFunction	Synonyms		
ReferenceFunction	GeneralComment	This report assumes that HCl is generated from combustion of chlorine with hydrogen	This report assumes that HCl is generated from combustion of chlorine with hydrogen. HCl is also produced as a by-product by several processes (TDI, MDI, fluorocarbons), for which no allocation was carried out, in part due to a lack of data.
ReferenceFunction	CASNumber	7647-01-0	7647-01-0
TimePeriod	StartDate	1997	1997
TimePeriod	EndDate	2000	2000
TimePeriod	DataValidForEntirePeriod	1	1
TimePeriod	OtherPeriodText		
Geography	Text	RER	RER
Technology	Text	represents a current cross-section of actual plants in Europe	based on literature data and plant data in Europe and North America
Representativeness	Percent		
Representativeness	ProductionVolume	unknown	unknown
Representativeness	SamplingProcedure	see technology	see technology
Representativeness	Extrapolations	see technology	see technology
Representativeness	UncertaintyAdjustments	none	none

41.11 References

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42 Hydrogen

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Review: Heiko Kunst, TU Berlin

Last Changes:

2007

42.1 Introduction

This chapter describes the production of hydrogen (H_2). This chemical is used primarily for the production of ammonia, methanol or is used as a fuel.

42.2 Reserves and resources of H_2

Hydrogen is a gaseous element. It is produced primarily from petroleum, coal and natural gas.

42.3 Characterisation of H_2

Hydrogen (H_2 , CAS 1333-74-0) is a colorless gas. Its molecular weight is 2.02 g/mol. Hydrogen boils at $-252.9\text{ }^{\circ}\text{C}$. Hydrogen is flammable and can act as a simple asphyxiant by displacing the oxygen in the air. In addition, when cooled to a liquid form, it may cause severe frostbite.

42.4 Production and use of H_2

In 1988, some 500 billion cubic meters of hydrogen were produced annually, according to Scholz (1992). Worldwide, 48% of hydrogen is produced from natural gas, 30% from oil (mostly consumed in refineries), 18% from coal, and the remaining (4%) via water electrolysis. Hydrogen is used primarily in the following applications¹:

- Commercial fixation of nitrogen from the air to produce ammonia for fertilizer (about two-thirds of commercial hydrogen is used for this)
- Hydrogenation of fats and oils, in which vegetable oils are changed from liquids to solids;
- Methanol production, in hydrodealkylation, hydrocracking, and hydrodesulphurization
- Welding
- Hydrochloric acid production
- Metallic ore reduction
- Hydrogen can be used in fuel cells to power a wide variety of applications (eg cars)

Major manufacturers include Linde, Air Liquide, and Praxair.

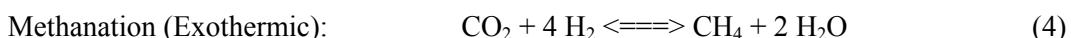
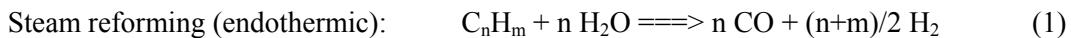
42.5 System characterization

Hydrogen can be produced at refineries by steam reforming of light ends or natural gas (the most common production route in Europe) or by partial oxidation (gasification) of heavy oil fractions (produces syngas, from which hydrogen can be separated). Hydrogen can also be produced by coal or coke gasification (European Commission (2001)).

¹ Information from Website <http://www.hydrogen.energy.gov/>

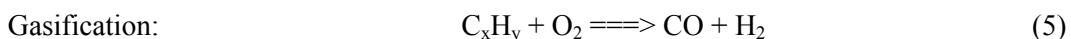
42.5.1 Steam reforming (European Commission (2001))

Natural gas, refinery gas and light naphtha are fed into a reactor and are heated to 760 - 840 °C and pressurized at 20 – 30 bar in the presence of a catalyst. Heat is provided by furnace burners. Steam is reacted with CO to produce carbon dioxide and hydrogen (shift reaction). The reformed gas is a mixture of hydrogen, carbon dioxide, carbon monoxide, methane and steam. The non-hydrogen components are removed and the resulting hydrogen has a purity of over 99.9% with a yield of approximately 85% (Scholz (1992)). Steam is raised to cool down the gases.



42.5.2 Partial oxidation

Hydrocarbon feed reacts with oxygen at high temperatures to produce a mixture of hydrogen and carbon monoxide. Due to the high temperature, there is no catalyst involved, which means that also heavy fuel oil feedstocks can be used. The gas is generated in a pressure vessel at about 1300 – 1400 °C. The resulting gases are cooled by direct-water quench. Soot and solid impurities are washed out. The hydrogen is 98.6% pure, with nitrogen, argon and methane as impurities (European Commission (2001)), (Scholz (1992)).



Source. European Commission (2001).

42.5.3 Gasification of coke / coal

Coke is reacted at 850 – 1000 °C with air and steam to form coke gas (a mixture of hydrogen, carbon monoxide, carbon dioxide and nitrogen). The cracked hydrocarbon vapor product is quenched. The hydrogen stems from water. Coal can also be used as feed. In such a case, the coal is pulverized and mixed with water to create a slurry (Scholz (1992)).



Source. European Commission (2001).

42.6 Hydrogen, from fossil fuels, at plant (RER)

The production process for hydrogen from fossil fuels was assessed with data from PlasticsEurope (Boustead (2005-07)), representing an average value from seventeen European plants. Due to the fact that this dataset is cumulated it was not possible to use the other processes modelled in ecoinvent to obtain a transparent process chain. The data was nevertheless used because it represents a high share of the European production of this type of chemicals. The transformation for the data as given in Boustead (2005-07) to the data format in ecoinvent is described in detail in the methodology part of the plastics part in Hischier (2007).

Within the module assessed here there are only the resources and emissions considered which are given in the data source. Therefore no land use could be included and no direct soil emissions within the process chain are stated. For each waste type used in the original dataset, an appropriate waste process from the ecoinvent modules was included.

42.7 Data quality considerations

Tab. 42.1 and Tab. 42.3 summarize the resulting data of the hydrogen production in Europe. According to the methodological remarks in Hischier (2007), these data contain no uncertainty information. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 42.11.

Tab. 42.1 Input data and functional unit outflow of the dataset for hydrogen production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	hydrogen, cracking, APME, at plant	RER 0 kg	uncertaintyType	standardDeviation05%	GeneralComment	
								Location	
								InfrastructureProcess	
								Unit	
Resources	401	Oil, crude, in ground	kg	7.56E-01				Uncertainty for LCI results cannot be determined	
		Gas, natural, in ground	Nm3	9.21E-01				Uncertainty for LCI results cannot be determined	
		Coal, hard, unspecified, in ground	kg	4.88E-02				Uncertainty for LCI results cannot be determined	
		Coal, brown, in ground	kg	2.80E-08				Uncertainty for LCI results cannot be determined	
		Peat, in ground	kg	3.95E-04				Uncertainty for LCI results cannot be determined	
		Wood, unspecified, standing	m3	4.04E-09				Uncertainty for LCI results cannot be determined	
		Energy, potential (in hydropower reservoir), converted	MJ	5.73E-02				Uncertainty for LCI results cannot be determined	
		Uranium, in ground	kg	2.62E-06				Uncertainty for LCI results cannot be determined	
		Energy, gross calorific value, in biomass	MJ	1.32E-01				Uncertainty for LCI results cannot be determined	
		Barite, 15% in crude ore, in ground	kg	3.01E-08				Uncertainty for LCI results cannot be determined	
		Aluminium, 24% in bauxite, 11% in crude ore, in ground	kg	3.70E-07				Uncertainty for LCI results cannot be determined	
		Clay, bentonite, in ground	kg	1.10E-04				Uncertainty for LCI results cannot be determined	
		Anhydrite, in ground	kg	1.10E-05				Uncertainty for LCI results cannot be determined	
		Calcite, in ground	kg	3.74E-04				Uncertainty for LCI results cannot be determined	
		Clay, unspecified, in ground	kg	1.90E-10				Uncertainty for LCI results cannot be determined	
		Chromium, 25.5 in chromite, 11.6% in crude ore, in ground	kg	3.70E-13				Uncertainty for LCI results cannot be determined	
		Copper, 0.99% in sulfide, Cu 0.36% and Mo 8.2E-3% in crude ore, in ground	kg	9.97E-12				Uncertainty for LCI results cannot be determined	
		Dolomite, in ground	kg	4.64E-06				Uncertainty for LCI results cannot be determined	
		Iron, 46% in ore, 25% in crude ore, in ground	kg	3.78E-04				Uncertainty for LCI results cannot be determined	
		Feldspar, in ground	kg	3.41E-16				Uncertainty for LCI results cannot be determined	
		Manganese, 35.7% in sedimentary deposit, 14.2% in crude ore, in ground	kg	4.87E-07				Uncertainty for LCI results cannot be determined	
		Fluorspar, 92%, in ground	kg	1.88E-07				Uncertainty for LCI results cannot be determined	
		Granite, in ground	kg	1.64E-15				Uncertainty for LCI results cannot be determined	
		Gravel, in ground	kg	1.39E-06				Uncertainty for LCI results cannot be determined	
		Cinnabar, in ground	kg	8.40E-10				Uncertainty for LCI results cannot be determined	
		Magnesite, 60% in crude ore, in ground	kg	5.42E-28				Uncertainty for LCI results cannot be determined	
		Nickel, 1.98% in silicates, 1.04% in crude ore, in ground	kg	4.74E-13				Uncertainty for LCI results cannot be determined	
		Olivine, in ground	kg	3.54E-06				Uncertainty for LCI results cannot be determined	
		Lead, 5.0% in sulfide, Pb 3.0%, Zn, Ag, Cd, In, in ground	kg	1.83E-07				Uncertainty for LCI results cannot be determined	
		Phosphorus, 18% in apatite, 12% in crude ore, in ground	kg	1.24E-12				Uncertainty for LCI results cannot be determined	
		Sylvite, 25 % in sylvinite, in ground	kg	4.45E-09				Uncertainty for LCI results cannot be determined	
		TiO2, 95% in rutile, 0.40% in crude ore, in ground	kg	3.82E-34				Uncertainty for LCI results cannot be determined	
		Sulfur, in ground	kg	9.09E-05				Uncertainty for LCI results cannot be determined	
		Sand, unspecified, in ground	kg	7.13E-05				Uncertainty for LCI results cannot be determined	
		Shale, in ground	kg	3.11E-05				Uncertainty for LCI results cannot be determined	
		Sodium chloride, in ground	kg	5.36E-04				Uncertainty for LCI results cannot be determined	
		sodium nitrate, in ground	kg	1.63E-27				Uncertainty for LCI results cannot be determined	
		Talc, in ground	kg	3.93E-28				Uncertainty for LCI results cannot be determined	
		Zinc, 9.0% in sulfide, Zn 5.3%, Pb, Ag, Cd, In, in ground	kg	6.67E-09				Uncertainty for LCI results cannot be determined	
		Water, unspecified natural origin	m3	7.23E-04				Uncertainty for LCI results cannot be determined	
		Water, river	m3	5.61E-04				Uncertainty for LCI results cannot be determined	
		Water, salt, ocean	m3	7.85E-04				Uncertainty for LCI results cannot be determined	
		Water, well, in ground	m3	9.01E-11				Uncertainty for LCI results cannot be determined	
		Water, cooling, unspecified natural origin	m3	7.32E-02				Uncertainty for LCI results cannot be determined	
		disposal, facilities, chemical production	kg	1.55E-09				Uncertainty for LCI results cannot be determined	
Input from Technosphere		disposal, hard coal mining waste tailings, in surface backfill	kg	9.90E-03				Uncertainty for LCI results cannot be determined	
		disposal, municipal solid waste, 22.9% water, to municipal incineration	kg	1.31E-03				Uncertainty for LCI results cannot be determined	
		disposal, average incineration residue, 0% water, to residual material landfill	kg	4.60E-03				Uncertainty for LCI results cannot be determined	
		disposal, wood untreated, 20% water, to municipal incineration	kg	5.32E-08				Uncertainty for LCI results cannot be determined	
		disposal, plastics, mixture, 15.3% water, to municipal incineration	kg	4.81E-07				Uncertainty for LCI results cannot be determined	
		disposal, hazardous waste, 0% water, to underground deposit	kg	1.57E-03				Uncertainty for LCI results cannot be determined	
Output		hydrogen, cracking, APME, at plant	kg	1.00E+00					

Tab. 42.2 Emission to air data for hydrogen production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	hydrogen, cracking, APME, at plant	RER 0 kg	uncertaintyType standardDeviation95%	GeneralComment	
							Location	InfrastructureProcess
							493	403
							Unit	
Air emission	Heat, waste		MJ	2.30E+01			Uncertainty for LCI results cannot be determined	
		Particulates, > 10 um	kg	1.38E-04			Uncertainty for LCI results cannot be determined	
		Particulates, > 2.5 um, and < 10um	kg	1.86E-04			Uncertainty for LCI results cannot be determined	
		Particulates, < 2.5 um	kg	1.08E-04			Uncertainty for LCI results cannot be determined	
Air emission	Carbon monoxide, fossil		kg	2.51E-03			Uncertainty for LCI results cannot be determined	
		Carbon monoxide, biogenic	kg	5.65E-06			Uncertainty for LCI results cannot be determined	
		Carbon dioxide, fossil	kg	1.23E+00			Uncertainty for LCI results cannot be determined	
		Carbon dioxide, biogenic	kg	2.78E-03			Uncertainty for LCI results cannot be determined	
Air emission	Sulfur dioxide		kg	2.03E-03			Uncertainty for LCI results cannot be determined	
		Hydrogen sulfide	kg	1.27E-08			Uncertainty for LCI results cannot be determined	
		Nitrogen oxides	kg	2.12E-03			Uncertainty for LCI results cannot be determined	
		Ammonia	kg	1.26E-10			Uncertainty for LCI results cannot be determined	
Air emission	Chlorine		kg	3.68E-11			Uncertainty for LCI results cannot be determined	
		Hydrogen chloride	kg	2.17E-05			Uncertainty for LCI results cannot be determined	
		Fluorine	kg	2.42E-11			Uncertainty for LCI results cannot be determined	
		Hydrogen fluoride	kg	8.14E-07			Uncertainty for LCI results cannot be determined	
Air emission	NMVOC, non-methane volatile organic compounds, unspecified origin		kg	2.10E-03			Uncertainty for LCI results cannot be determined	
		Aldehydes, unspecified	kg	5.22E-16			Uncertainty for LCI results cannot be determined	
		Lead	kg	1.04E-09			Uncertainty for LCI results cannot be determined	
		Mercury	kg	2.15E-09			Uncertainty for LCI results cannot be determined	
Air emission	Sulfate		kg	6.09E-15			Uncertainty for LCI results cannot be determined	
		Dinitrogen monoxide	kg	2.76E-13			Uncertainty for LCI results cannot be determined	
		Hydrogen	kg	3.04E-05			Uncertainty for LCI results cannot be determined	
		Ethane, 1,2-dichloro-	kg	7.96E-12			Uncertainty for LCI results cannot be determined	
Air emission	Ethene, chloro-		kg	1.78E-10			Uncertainty for LCI results cannot be determined	
		Halogenated hydrocarbons, chlorinated	kg	5.22E-09			Uncertainty for LCI results cannot be determined	
		Cyanide	kg	2.71E-18			Uncertainty for LCI results cannot be determined	
		Methane, fossil	kg	1.82E-02			Uncertainty for LCI results cannot be determined	
Air emission	Methane, biogenic		kg	4.09E-05			Uncertainty for LCI results cannot be determined	
		Hydrocarbons, aromatic	kg	7.63E-06			Uncertainty for LCI results cannot be determined	
		Hydrocarbons, aliphatic, alkanes, cyclic	kg	5.88E-18			Uncertainty for LCI results cannot be determined	
		Carbon disulfide	kg	8.08E-11			Uncertainty for LCI results cannot be determined	
Air emission	Methane, dichloro-, HCC-30		kg	5.98E-14			Uncertainty for LCI results cannot be determined	
		Copper	kg	2.79E-14			Uncertainty for LCI results cannot be determined	
		Arsenic	kg	1.53E-10			Uncertainty for LCI results cannot be determined	
		Cadmium	kg	2.44E-11			Uncertainty for LCI results cannot be determined	
Air emission	Silver		kg	1.26E-23			Uncertainty for LCI results cannot be determined	
		Zinc	kg	4.08E-11			Uncertainty for LCI results cannot be determined	
		Chromium	kg	6.96E-10			Uncertainty for LCI results cannot be determined	
		Selenium	kg	4.35E-25			Uncertainty for LCI results cannot be determined	
Air emission	Nickel		kg	4.99E-14			Uncertainty for LCI results cannot be determined	
		Antimony	kg	2.08E-15			Uncertainty for LCI results cannot be determined	
		Ethene	kg	3.41E-14			Uncertainty for LCI results cannot be determined	
		Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin	kg	1.30E-31			Uncertainty for LCI results cannot be determined	
Air emission	Benzene		kg	1.45E-17			Uncertainty for LCI results cannot be determined	
		Toluene	kg	2.43E-18			Uncertainty for LCI results cannot be determined	
		Xylene	kg	1.12E-18			Uncertainty for LCI results cannot be determined	
		Benzene, ethyl-	kg	8.52E-19			Uncertainty for LCI results cannot be determined	
Air emission	Styrene		kg	1.20E-19			Uncertainty for LCI results cannot be determined	
		Propene	kg	1.60E-17			Uncertainty for LCI results cannot be determined	

Tab. 42.3 Emission to water data for hydrogen production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	hydrogen, cracking, APME, at plant	RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment	
Water emission	662	Location							
	493	InfrastructureProcess							
	403	Unit							
	COD, Chemical Oxygen Demand	kg	1.53E-04					Uncertainty for LCI results cannot be determined	
	BOD ₅ , Biological Oxygen Demand	kg	3.68E-05					Uncertainty for LCI results cannot be determined	
	Lead	kg	2.67E-10					Uncertainty for LCI results cannot be determined	
	Iron, ion	kg	1.61E-08					Uncertainty for LCI results cannot be determined	
	Sodium, ion	kg	1.62E-04					Uncertainty for LCI results cannot be determined	
	Acidity, unspecified	kg	9.95E-07					Uncertainty for LCI results cannot be determined	
	Nitrate	kg	5.84E-06					Uncertainty for LCI results cannot be determined	
	Mercury	kg	3.20E-10					Uncertainty for LCI results cannot be determined	
	Ammonium, ion	kg	1.76E-06					Uncertainty for LCI results cannot be determined	
	Chloride	kg	7.40E-05					Uncertainty for LCI results cannot be determined	
	Cyanide	kg	3.58E-11					Uncertainty for LCI results cannot be determined	
	Fluoride	kg	1.35E-09					Uncertainty for LCI results cannot be determined	
	Sulfide	kg	2.04E-13					Uncertainty for LCI results cannot be determined	
	Hydrocarbons, unspecified	kg	2.23E-05					Uncertainty for LCI results cannot be determined	
	Suspended solids, unspecified	kg	1.27E-04					Uncertainty for LCI results cannot be determined	
	Oils, unspecified	kg	2.00E-05					Uncertainty for LCI results cannot be determined	
	Chlorinated solvents, unspecified	kg	7.06E-09					Uncertainty for LCI results cannot be determined	
	Chlorine	kg	8.41E-10					Uncertainty for LCI results cannot be determined	
	Phenol	kg	1.15E-06					Uncertainty for LCI results cannot be determined	
	Solved solids	kg	1.52E-05					Uncertainty for LCI results cannot be determined	
	Phosphorus	kg	5.46E-08					Uncertainty for LCI results cannot be determined	
	Nitrogen	kg	4.24E-06					Uncertainty for LCI results cannot be determined	
	Sulfate	kg	4.83E-04					Uncertainty for LCI results cannot be determined	
	Ethane, 1,2-dichloro-	kg	1.81E-13					Uncertainty for LCI results cannot be determined	
	Ethene, chloro-	kg	3.30E-12					Uncertainty for LCI results cannot be determined	
	Potassium, ion	kg	1.30E-10					Uncertainty for LCI results cannot be determined	
	Calcium, ion	kg	3.52E-08					Uncertainty for LCI results cannot be determined	
	Magnesium	kg	4.95E-10					Uncertainty for LCI results cannot be determined	
	Chromium, ion	kg	7.38E-14					Uncertainty for LCI results cannot be determined	
	Chlorate	kg	1.19E-07					Uncertainty for LCI results cannot be determined	
	Bromate	kg	4.34E-10					Uncertainty for LCI results cannot be determined	
	TOC, Total Organic Carbon	kg	5.25E-05					Uncertainty for LCI results cannot be determined	
	AOX, Adsorbable Organic Halogen as Cl	kg	5.05E-13					Uncertainty for LCI results cannot be determined	
	Aluminum	kg	1.41E-06					Uncertainty for LCI results cannot be determined	
	Zinc, ion	kg	8.28E-08					Uncertainty for LCI results cannot be determined	
	Copper, ion	kg	1.65E-08					Uncertainty for LCI results cannot be determined	
	Nickel, ion	kg	4.57E-10					Uncertainty for LCI results cannot be determined	
	Carbonate	kg	1.73E-04					Uncertainty for LCI results cannot be determined	
	Arsenic, ion	kg	8.30E-10					Uncertainty for LCI results cannot be determined	
	Cadmium, ion	kg	4.44E-15					Uncertainty for LCI results cannot be determined	
	Manganese	kg	2.24E-14					Uncertainty for LCI results cannot be determined	
	Tin, ion	kg	2.44E-16					Uncertainty for LCI results cannot be determined	
	Strontium	kg	1.29E-11					Uncertainty for LCI results cannot be determined	
	Silicon	kg	1.69E-19					Uncertainty for LCI results cannot be determined	
	Benzene	kg	1.91E-21					Uncertainty for LCI results cannot be determined	
	Molybdenum	kg	-					Uncertainty for LCI results cannot be determined	

42.8 Hydrogen, production mix, at plant (RER)

As nearly 5% of all hydrogen is produced from the electrolysis of sodium chloride (chlorine production, see chapter 24 of this report here) the following inventory – representing the production mix of hydrogen in Europe – incorporates this hydrogen production route as well. Again, the most important fields of the ecospold meta information are listed in chapter 42.11.

Tab. 42.4 Input / output data and data quality for hydrogen in Europe (production mix from fossil fuels and salt brine electrolysis)

Explanations	Name	Location	Unit	hydrogen, liquid, at plant	Uncertainty Type	Standard Deviation 95%	General Comment
	Location			RER			
	Infrastructure Process			0			
	Unit			kg			
Input from Technosphere	hydrogen, cracking, APME, at plant	RER	kg	9.50E-01	1	1.12	(1,3,1,1,1,4); hydrogen from cracking of fossil fuels
Outputs	hydrogen, liquid, from chlorine electrolysis, production mix, at plant	RER	kg	5.00E-02	1	1.12	(1,3,1,1,1,4); hydrogen from electrolysis of salt brine
	hydrogen, liquid, at plant	RER	kg	1			

42.9 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

42.10 Conclusions

The inventory data used in this process does not give transparency on the processes used and allocations made due to the use of cumulated data. Therefore, many emissions especially soil emissions are not accounted. Because of the cumulated data also no land occupation and land transformation could be included in the dataset. This leads to an incompleteness of the dataset, which has to be considered when using it. Also the uncertainty of the data used could not be determined for those datasets. Nevertheless the data refers on a large share of the European production and should therefore be representative for the production of this chemical.

42.11 EcoSpold Meta Information

ReferenceFunction	401 Name	hydrogen, cracking, APME, at plant	hydrogen, liquid, at plant
Geography	662 Location	RER	RER
ReferenceFunction	493 InfrastructureProcess	0	0
ReferenceFunction	403 Unit	kg	kg
ReferenceFunction	402 IncludedProcesses	Aggregated data for all processes from raw material extraction until delivery at plant	
ReferenceFunction	404 Amount	1	1
ReferenceFunction	490 LocalName	Wasserstoff, Cracker, APME, ab Werk	Wasserstoff, flüssig, ab Werk
ReferenceFunction	491 Synonyms		
ReferenceFunction	492 GeneralComment	Data are from the Eco-profiles of the European plastics industry (PlasticsEurope). Not included are the values reported for: recyclable wastes, amount of air / N2 / O2 consumed, unspecified metal emission to air and to water, mercaptan emission to air, unspecified CFC/HCFC emission to air, dioxin to water. The amount of "sulphur (bonded)" is assumed to be included into the amount of raw oil.	Data are from the Eco-profiles of the European plastics industry (PlasticsEurope). Not included are the values reported for: recyclable wastes, amount of air / N2 / O2 consumed, unspecified metal emission to air and to water, mercaptan emission to air, unspecified CFC/HCFC emission to air, dioxin to water. The amount of "sulphur (bonded)" is assumed to be included into the amount of raw oil.
ReferenceFunction	502 CASNumber	1333-74-0	1333-74-0
TimePeriod	601 StartDate	1999	1997
TimePeriod	602 EndDate	2001	2000
TimePeriod	603 DataValidForEntirePeriod	1	1
TimePeriod	611 OtherPeriodText	time to which data refer	
Geography	663 Text	17 European plants	RER
Technology	692 Text	production during cracking of naphtha	based on literature data
Representativeness	722 Percent		
Representativeness	724 ProductionVolume	worldwide 240 billion m3 in 1988	unknown
Representativeness	725 SamplingProcedure	literature values based on company survey	see technology
Representativeness	726 Extrapolations	no extrapolation	see technology
Representativeness	727 UncertaintyAdjustments	none	none

42.12 References

Boustead (2005-07)

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43 Hydrogen cyanide

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 Roland Hischier, Empa, St. Gallen (Changes 2007)

Review: Heiko Kunst, TU Berlin

Last Changes: 2007

43.1 Introduction

This chapter describes the production of hydrogen cyanide (HCN). This chemical is used primarily for the production of synthetic fibers, plastics and nitrites.

Synonyms for hydrogen cyanide: prussic acid, hydrocyanic acid

43.2 Reserves and resources of HCN

Hydrogen cyanide is a nitrogen-containing organic chemical compound. It is produced from the reaction of methane (natural gas) with ammonia.

43.3 Characterisation of HCN

HCN is a highly volatile and highly toxic colorless liquid that produces poisonous vapors at room temperature (almond odor). Its molecular weight is 27.03 g/mol. HCN melts at -13.2 °C, and boils just above 25°C. (US-EPA (2000))

43.4 Production and use of HCN

Historically, HCN gained notoriety for its use as Cyclon B at the Nazi death camps during World War II. It was produced at that time by DeGussa (Deutsche Gold- und Silberscheide-Anstalt). Sodium cyanide continued down HCN's path to notoriety by being mining companies choice chemical used to extract gold from ore. However, poor practices led to massive environmental contamination in several countries over the past decades².

The worldwide cyanide production capacity in 1994 was one million tonnes. DuPont is reported to be the dominant producer with close to 40% of production capacity.²

According to US-EPA (2000), the U.S. produced about 1.4 billion pounds (645'000 tonnes) in 1998. US production had the following uses:

Tab. 43.1 1998 US HCN production and uses (US-EPA (2000))

	Share (%)
Adiponitrile (for nylon)	41
Acetone cyanohydrin (for methyl methacrylate MMA)	32
Sodium cyanide	14
methionine	4
miscellaneous	9

Major manufacturers include Cyanco, DeGussa-Huls Corp., Dow Chemical Co. and DuPont.

² Information taken from http://www.moles.org/ProjectUnderground/reports/goldpack/goldpack_i.html

In 1997-2000, European production of toluene was approximately 2.7 million tons; according to (European Commission (2002)). Major plants are operated in Germany, the Netherlands, Italy, Spain, the UK, the US, Japan, Taiwan, South Korea, among others. Major manufacturers include DeGussa, Dow and DuPont.

43.5 System characterization

HCN is produced mostly from the so-called Andrussov and Blausäure-Methan-Ammoniak (BMA) process, although some HCN is also obtained as a by-product from acrylonitrile production (US-EPA (2000)).

43.5.1 Andrussov process (US-EPA (2000))

Filtered air, ammonia and natural gas are fed into a reactor and are heated to 2'200 °C in the presence of a catalyst. The reactor off-gas is cooled and sent through an ammonia absorption process to remove unreacted ammonia. Cold water is then added to capture the HCN. The HCN-water mixture is sent to a stripper, where pure HCN is gained. This step produces wastewater.



43.5.2 Blausaure-Methan-Ammonia Process (US-EPA (2000))

The BMA process involves the reaction of ammonia with methane without the presence of air. After removal of ammonia and recovery of HCN, the off-gases consist basically of hydrogen. The hydrogen can be used in other processes or burnt as a source of energy.



BMA accounts for 15 % of the total European production.³

Resource consumption

Tab. 43.2 Resource consumption for the production of HCN (kg/kg)

Precursor	Amount (kg)
Ammonia	0.76
Natural gas	0.68
Sulfuric acid (conc.)	0.26

In case the hydrogen produced by the BMA process is not combusted, a total of 0.23 kg hydrogen is produced per kg HCN.

³ Personal communication Ramon Mendivil, ETH Zurich Institute for Chemical- and Bioengineering, Safety & Environmental Technology Group, May/June 2003.

Energy consumption

Tab. 43.3 Energy consumption for the production of HCN (kg/kg)

Precursor	Hydrogen export route	Hydrogen combustion route
Natural gas	0.78	0.51

A total of 31 MJ is required per kg of HCN.

Air emissions (BMA process)

Tab. 43.4 Air emissions from the production of HCN (g/kg)

Substance	Amount (g)
Dust (SPM)	1.01
SOx	18.82
CH4	0.98
NOx	9.30
CO2	2473.52

These figures – numbers from ⁴ – are calculated values based on the combustion of hydrogen gas in the process as a fuel that replaces part of the natural gas burned as a fuel.

Wastewater / Liquid wastes

No values available.

Solid wastes (BMA process)

0.34 kg of ammonium sulfate (Na_2SO_4) are produced per kg of HCN, as well as 0.02 kg of sodium cyanide. The ammonium sulfate is sold as a fertilizer.⁴

43.6 Life cycle Inventory for HCN

The production process for hydrogen cyanide was assessed with data from PlasticsEurope (Boustead (2005-07)), that is based on the years 1992 – 1993 and accounts for about 63'000 tons of HCN produced at three sites in Europe. It cannot be ascertained which processes were used by the companies providing the data – the hydrogen emissions that are listed are no indicator of the actual processes, as hydrogen stemming from the BMA process may be captured and used in other processes and still cause emissions.

Due to the fact that the PlasticsEurope dataset is cumulated it was not possible to use the other processes modelled in ecoinvent to obtain a transparent process chain. The data was nevertheless used because it represents a high share of the European production of this type of chemicals. The transforma-

⁴ Personal communication Ramon Mendivil, ETH Zurich Institute for Chemical- and Bioengineering, Safety & Environmental Technology Group, May/June 2003.

tion for the data as given in Boustead (2005-07) to the data format in ecoinvent is described in detail in the methodology part of the plastics part in Hischier (2007).

Within the module assessed here there are only the resources and emissions considered which are given in the data source. Therefore no land use could be included and no direct soil emissions within the process chain are stated. For each waste type used in the original dataset, an appropriate waste process from the ecoinvent modules was included.

43.7 Data quality considerations

Tab. 43.5 and Tab. 43.7 summarize the resulting data of the HCN production in Europe. According to the methodological remarks in Hischier (2007), these data contain no uncertainty information. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 43.11.

Tab. 43.5 Input data and functional unit outflow of the dataset for HCN production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	hydrogen cyanide, at plant	uncertaintyType	standardDeviations95%	GeneralComment
	662	Location		RER			
	493	InfrastructureProcess		o			
	403	Unit		kg			
Resources		Oil, crude, in ground	kg	3.10E-01			Uncertainty for LCI results cannot be determined
		Gas, natural, in ground	Nm3	2.41E+00			Uncertainty for LCI results cannot be determined
		Coal, hard, unspecified, in ground	kg	1.65E-01			Uncertainty for LCI results cannot be determined
		Coal, brown, in ground	kg	1.80E-06			Uncertainty for LCI results cannot be determined
		Peat, in ground	kg	1.07E-05			Uncertainty for LCI results cannot be determined
		Wood, unspecified, standing	m3	6.18E-08			Uncertainty for LCI results cannot be determined
		Energy, potential (in hydropower reservoir), converted	MJ	5.38E-01			Uncertainty for LCI results cannot be determined
		Uranium, in ground	kg	7.87E-06			Uncertainty for LCI results cannot be determined
		Energy, gross calorific value, in biomass	MJ	3.40E-01			Uncertainty for LCI results cannot be determined
		Barite, 15% in crude ore, in ground	kg	5.14E-07			Uncertainty for LCI results cannot be determined
		Aluminium, 24% in bauxite, 11% in crude ore, in ground	kg	6.30E-05			Uncertainty for LCI results cannot be determined
		Clay, bentonite, in ground	kg	9.62E-08			Uncertainty for LCI results cannot be determined
		Anhydrite, in ground	kg	1.55E-09			Uncertainty for LCI results cannot be determined
		Calcite, in ground	kg	1.39E-03			Uncertainty for LCI results cannot be determined
		Clay, unspecified, in ground	kg	2.38E-09			Uncertainty for LCI results cannot be determined
		Chromium, 25.5% in chromite, 11.6% in crude ore, in ground	kg	1.82E-12			Uncertainty for LCI results cannot be determined
		Copper, 0.99% in sulfide, Cu 0.36% and Mo 8.2E-3% in crude ore, in ground	kg	8.83E-11			Uncertainty for LCI results cannot be determined
		Dolomite, in ground	kg	1.42E-06			Uncertainty for LCI results cannot be determined
		Iron, 46% in ore, 25% in crude ore, in ground	kg	1.16E-04			Uncertainty for LCI results cannot be determined
		Feldspar, in ground	kg	2.78E-20			Uncertainty for LCI results cannot be determined
		Manganese, 35.7% in sedimentary deposit, 14.2% in crude ore, in ground	kg	1.50E-07			Uncertainty for LCI results cannot be determined
		Fluorspar, 92%, in ground	kg	1.65E-05			Uncertainty for LCI results cannot be determined
		Granite, in ground	kg	7.95E-15			Uncertainty for LCI results cannot be determined
		Gravel, in ground	kg	4.28E-07			Uncertainty for LCI results cannot be determined
		Cinnabar, in ground	kg	1.41E-08			Uncertainty for LCI results cannot be determined
		Magnesite, 60% in crude ore, in ground	kg	9.26E-21			Uncertainty for LCI results cannot be determined
		Nickel, 1.98% in silicates, 1.04% in crude ore, in ground	kg	5.65E-11			Uncertainty for LCI results cannot be determined
		Olivine, in ground	kg	1.09E-06			Uncertainty for LCI results cannot be determined
		Lead, 5.0% in sulfide, Pb 3.0%, Zn, Ag, Cd, In, in ground	kg	8.92E-07			Uncertainty for LCI results cannot be determined
		Phosphorus, 18% in apatite, 12% in crude ore, in ground	kg	2.62E-03			Uncertainty for LCI results cannot be determined
		Sylvite, 25 % in sylvinitre, in ground	kg	1.36E-06			Uncertainty for LCI results cannot be determined
		TiO2, 95% in rutile, 0.40% in crude ore, in ground	kg	1.86E-33			Uncertainty for LCI results cannot be determined
		Sulfur, in ground	kg	2.21E-02			Uncertainty for LCI results cannot be determined
		Sand, unspecified, in ground	kg	1.13E-02			Uncertainty for LCI results cannot be determined
		Shale, in ground	kg	4.40E-09			Uncertainty for LCI results cannot be determined
		Sodium chloride, in ground	kg	7.22E-03			Uncertainty for LCI results cannot be determined
		sodium nitrate, in ground	kg	2.78E-20			Uncertainty for LCI results cannot be determined
		Talc, in ground	kg	4.72E-27			Uncertainty for LCI results cannot be determined
		Zinc, 9.0% in sulfide, Zn 5.3%, Pb, Ag, Cd, In, in ground	kg	3.26E-08			Uncertainty for LCI results cannot be determined
		Water, unspecified natural origin	m3	1.35E-02			Uncertainty for LCI results cannot be determined
		Water, river	m3	1.95E-03			Uncertainty for LCI results cannot be determined
		Water, salt, ocean	m3	6.87E-08			Uncertainty for LCI results cannot be determined
		Water, well, in ground	m3	3.85E-04			Uncertainty for LCI results cannot be determined
		Water, cooling, unspecified natural origin	m3	7.13E-02			Uncertainty for LCI results cannot be determined
Input from Technosphere		disposal, facilities, chemical production	kg	1.63E-09			Uncertainty for LCI results cannot be determined
		disposal, hard coal mining waste tailings, in surface backfill	kg	3.54E-02			Uncertainty for LCI results cannot be determined
		disposal, municipal solid waste, 22.9% water, to municipal incineration	kg	7.89E-03			Uncertainty for LCI results cannot be determined
		disposal, average incineration residue, 0% water, to residual material landfill	kg	4.20E-02			Uncertainty for LCI results cannot be determined
		disposal, wood untreated, 20% water, to municipal incineration	kg	8.13E-07			Uncertainty for LCI results cannot be determined
		disposal, plastics, mixture, 15.3% water, to municipal incineration	kg	7.19E-06			Uncertainty for LCI results cannot be determined
		disposal, hazardous waste, 0% water, to underground deposit	kg	9.55E-03			Uncertainty for LCI results cannot be determined
Output		hydrogen cyanide, at plant	kg	1.00E+00			

Tab. 43.6 Emission to air data for HCN production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	hydrogen cyanide, at plant		standardDeviation95%	GeneralComment
				RER	0 kg		
Air emission	662	Location					
	493	Infrastructure					
	403	Process					
		Unit					
		Heat, waste	MJ	6.27E+01			Uncertainty for LCI results cannot be determined
		Particulates, > 10 um	kg	5.19E-04			Uncertainty for LCI results cannot be determined
		Particulates, > 2.5 um, and < 10um	kg	6.97E-04			Uncertainty for LCI results cannot be determined
		Particulates, < 2.5 um	kg	4.05E-04			Uncertainty for LCI results cannot be determined
		Carbon monoxide, fossil	kg	4.11E-03			Uncertainty for LCI results cannot be determined
		Carbon monoxide, biogenic	kg	5.32E-06			Uncertainty for LCI results cannot be determined
		Carbon dioxide, fossil	kg	4.69E+00			Uncertainty for LCI results cannot be determined
		Carbon dioxide, biogenic	kg	6.07E-03			Uncertainty for LCI results cannot be determined
		Sulfur dioxide	kg	8.42E-03			Uncertainty for LCI results cannot be determined
		Hydrogen sulfide	kg	3.88E-09			Uncertainty for LCI results cannot be determined
		Nitrogen oxides	kg	7.31E-03			Uncertainty for LCI results cannot be determined
		Ammonia	kg	1.08E-04			Uncertainty for LCI results cannot be determined
		Chlorine	kg	1.60E-07			Uncertainty for LCI results cannot be determined
		Hydrogen chloride	kg	9.03E-05			Uncertainty for LCI results cannot be determined
		Fluorine	kg	3.23E-09			Uncertainty for LCI results cannot be determined
		Hydrogen fluoride	kg	3.39E-06			Uncertainty for LCI results cannot be determined
		NMVOC, non-methane volatile organic compounds, unspecified origin	kg	3.99E-03			Uncertainty for LCI results cannot be determined
		Aldehydes, unspecified	kg	2.50E-15			Uncertainty for LCI results cannot be determined
		Lead	kg	1.95E-10			Uncertainty for LCI results cannot be determined
		Mercury	kg	2.16E-09			Uncertainty for LCI results cannot be determined
		Sulfate	kg	8.74E-14			Uncertainty for LCI results cannot be determined
		Dinitrogen monoxide	kg	1.54E-12			Uncertainty for LCI results cannot be determined
		Hydrogen	kg	7.95E-05			Uncertainty for LCI results cannot be determined
		Ethane, 1,2-dichloro-	kg	3.89E-11			Uncertainty for LCI results cannot be determined
		Ethene, chloro-	kg	8.74E-10			Uncertainty for LCI results cannot be determined
		Halogenated hydrocarbons, chlorinated	kg	1.29E-09			Uncertainty for LCI results cannot be determined
		Cyanide	kg	4.80E-05			Uncertainty for LCI results cannot be determined
		Methane, fossil	kg	1.02E-01			Uncertainty for LCI results cannot be determined
		Methane, biogenic	kg	1.32E-04			Uncertainty for LCI results cannot be determined
		Hydrocarbons, aromatic	kg	7.42E-07			Uncertainty for LCI results cannot be determined
		Hydrocarbons, aliphatic, alkanes, cyclic	kg	7.97E-11			Uncertainty for LCI results cannot be determined
		Carbon disulfide	kg	1.13E-14			Uncertainty for LCI results cannot be determined
		Methane, dichloro-, HCC-30	kg	4.17E-10			Uncertainty for LCI results cannot be determined
		Copper	kg	1.77E-13			Uncertainty for LCI results cannot be determined
		Arsenic	kg	1.31E-11			Uncertainty for LCI results cannot be determined
		Cadmium	kg	1.93E-11			Uncertainty for LCI results cannot be determined
		Silver	kg	2.15E-16			Uncertainty for LCI results cannot be determined
		Zinc	kg	1.99E-10			Uncertainty for LCI results cannot be determined
		Chromium	kg	1.03E-10			Uncertainty for LCI results cannot be determined
		Selenium	kg	7.44E-18			Uncertainty for LCI results cannot be determined
		Nickel	kg	7.99E-11			Uncertainty for LCI results cannot be determined
		Antimony	kg	1.53E-14			Uncertainty for LCI results cannot be determined
		Ethene	kg	6.72E-11			Uncertainty for LCI results cannot be determined
		Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin	kg	1.97E-35			Uncertainty for LCI results cannot be determined
		Benzene	kg	1.78E-10			Uncertainty for LCI results cannot be determined
		Toluene	kg	3.18E-11			Uncertainty for LCI results cannot be determined
		Xylene	kg	1.42E-11			Uncertainty for LCI results cannot be determined
		Benzene, ethyl-	kg	1.45E-11			Uncertainty for LCI results cannot be determined
		Styrene	kg	1.23E-12			Uncertainty for LCI results cannot be determined
		Propene	kg	4.96E-11			Uncertainty for LCI results cannot be determined

Tab. 43.7 Emission to water data for HCN production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	hydrogen cyanide, at plant	uncertaintyType	standardDeviation95%	GeneralComment
	662	Location		RER			
	493	Infrastructure		0			
	403	Process	Unit	kg			
Water emission	COD, Chemical Oxygen Demand		kg	7.21E-04			Uncertainty for LCI results cannot be determined
	BOD5, Biological Oxygen Demand		kg	4.98E-05			Uncertainty for LCI results cannot be determined
	Lead		kg	1.88E-10			Uncertainty for LCI results cannot be determined
	Iron, ion		kg	6.70E-09			Uncertainty for LCI results cannot be determined
	Sodium, ion		kg	9.05E-04			Uncertainty for LCI results cannot be determined
	Acidity, unspecified		kg	1.00E-04			Uncertainty for LCI results cannot be determined
	Nitrate		kg	3.35E-05			Uncertainty for LCI results cannot be determined
	Mercury		kg	3.36E-10			Uncertainty for LCI results cannot be determined
	Ammonium, ion		kg	9.74E-04			Uncertainty for LCI results cannot be determined
	Chloride		kg	4.15E-03			Uncertainty for LCI results cannot be determined
	Cyanide		kg	4.33E-05			Uncertainty for LCI results cannot be determined
	Fluoride		kg	6.00E-06			Uncertainty for LCI results cannot be determined
	Sulfide		kg	1.01E-12			Uncertainty for LCI results cannot be determined
	Hydrocarbons, unspecified		kg	1.67E-05			Uncertainty for LCI results cannot be determined
	Suspended solids, unspecified		kg	9.55E-04			Uncertainty for LCI results cannot be determined
	Oils, unspecified		kg	7.30E-09			Uncertainty for LCI results cannot be determined
	Chlorinated solvents, unspecified		kg	1.08E-07			Uncertainty for LCI results cannot be determined
	Chlorine		kg	4.28E-09			Uncertainty for LCI results cannot be determined
	Phenol		kg	6.03E-09			Uncertainty for LCI results cannot be determined
	Solved solids		kg	7.93E-04			Uncertainty for LCI results cannot be determined
	Phosphorus		kg	4.14E-04			Uncertainty for LCI results cannot be determined
	Nitrogen		kg	2.66E-07			Uncertainty for LCI results cannot be determined
	Sulfate		kg	2.54E-03			Uncertainty for LCI results cannot be determined
	Ethane, 1,2-dichloro-		kg	8.82E-13			Uncertainty for LCI results cannot be determined
	Ethene, chloro-		kg	1.61E-11			Uncertainty for LCI results cannot be determined
	Potassium, ion		kg	4.26E-08			Uncertainty for LCI results cannot be determined
	Calcium, ion		kg	5.91E-07			Uncertainty for LCI results cannot be determined
	Magnesium		kg	9.40E-10			Uncertainty for LCI results cannot be determined
	Chromium, ion		kg	1.61E-10			Uncertainty for LCI results cannot be determined
	Chlorate		kg	1.83E-06			Uncertainty for LCI results cannot be determined
	Bromate		kg	5.63E-10			Uncertainty for LCI results cannot be determined
	TOC, Total Organic Carbon		kg	1.00E-06			Uncertainty for LCI results cannot be determined
	AOX, Adsorbable Organic Halogen as Cl		kg	4.24E-12			Uncertainty for LCI results cannot be determined
	Aluminum		kg	1.32E-07			Uncertainty for LCI results cannot be determined
	Zinc, ion		kg	1.98E-07			Uncertainty for LCI results cannot be determined
	Copper, ion		kg	1.18E-07			Uncertainty for LCI results cannot be determined
	Nickel, ion		kg	7.94E-08			Uncertainty for LCI results cannot be determined
	Carbonate		kg	8.78E-07			Uncertainty for LCI results cannot be determined
	Arsenic, ion		kg	5.97E-11			Uncertainty for LCI results cannot be determined
	Cadmium, ion		kg	3.34E-14			Uncertainty for LCI results cannot be determined
	Manganese		kg	2.38E-13			Uncertainty for LCI results cannot be determined
	Tin, ion		kg	1.80E-15			Uncertainty for LCI results cannot be determined
	Strontium		kg	2.03E-10			Uncertainty for LCI results cannot be determined
	Silicon		kg	1.36E-23			Uncertainty for LCI results cannot be determined
	Benzene		kg	2.67E-12			Uncertainty for LCI results cannot be determined
	Molybdenum		kg	-			Uncertainty for LCI results cannot be determined

43.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

43.9 Conclusions

The inventory data used in this process does not give transparency on the processes used and allocations made due to the use of cumulated data. Therefore, many emissions especially soil emissions are not accounted. Because of the cumulated data also no land occupation and land transformation could be included in the dataset. This leads to an incompleteness of the dataset, which has to be considered when using it. Also the uncertainty of the data used could not be determined for those datasets. Nevertheless the data refers on a large share of the European production and should therefore be representative for the production of this chemical.

43.10 EcoSpold Meta Information

ReferenceFunction	401	Name	hydrogen cyanide, at plant
Geography	662	Location	RER
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	402	IncludedProcesses	Aggregated data for all processes from raw material extraction until delivery at plant
ReferenceFunction	404	Amount	1
ReferenceFunction	490	LocalName	Cyanidwasserstoff, ab Werk
ReferenceFunction	491	Synonyms	
ReferenceFunction	492	GeneralComment	Data are from the Eco-profiles of the European plastics industry (PlasticsEurope). Not included are the values reported for: recyclable wastes, amount of air / N ₂ / O ₂ consumed, unspecified metal emission to air and to water, mercaptan emission to air, unspecified CFC/HCFC emission to air, dioxin to water. The amount of "sulphur (bonded)" is assumed to be included into the amount of raw oil.
ReferenceFunction	502	CASNumber	74-90-8
TimePeriod	601	StartDate	1992
TimePeriod	602	EndDate	2001
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	time to which data refer
Geography	663	Text	3 European plants (GB, F, D)
Technology	692	Text	production by reaction of methane with ammonia
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	worldwide capacity 1994 1 Mt
Representativeness	725	SamplingProcedure	literature values based on company survey
Representativeness	726	Extrapolations	no extrapolation
Representativeness	727	UncertaintyAdjustments	none

43.11 References

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44 Hydrogen Peroxide and Anthraquinone

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 Review: Heiko Kunst, TU Berlin

44.1 Introduction

Hydrogen peroxide (H_2O_2 , CAS-No. 7722-84-1) is a colourless liquid with a slightly sharp odour at higher concentrations. Hydrogen peroxide is used unique as an aqueous solution - in fact, it is miscible with water in all proportions. It decomposes exothermally to water and oxygen, either when heated over 80°C or in the presence of a variety of catalysts - e.g. methals, acids, oxidizable organic materials. The most important chemical and physical properties are summarized the table below.

Synonyms for H_2O_2 : dihydrogen dioxide; Hydroperoxide; Hioxy; Oxydol; Perhydrol; Peroxan; peroxide; hydrogen dioxide

Tab. 44.1 Chemical and physical properties of hydrogen peroxide (Chemfinder (2002)).

Property	Value	Unit	Property	Value	Unit
Molecular weight	34.015	g mol^{-1}	Melting point	-11	°C
Density (at 25°C)	1.41	g cm^{-3}	Boiling point	150.2	°C

44.2 Reserves and Resources

As shown in the chapter about the production, hydrogen peroxide is nowadays primary produced out of hydrogen with the aid of an anthraquinone. Therefore, its resources are similar like for hydrogen (see chapter 0).

44.3 Production Technologies and Use

44.3.1 Production technologies for hydrogen peroxide

Most common technique for the production of hydrogen peroxide is the autoxidation (AO) or anthraquinone process. Hydrogen peroxide is produced there by reducing alkylanthraquinone with hydrogen in the presence of a catalyst to the hydrochinone. Then the catalyst is removed and the hydrochinone is oxidised – usually with air – back to the origin quinone and in the same time hydrogen peroxide is produced. The quinones can than go back and are re-hydrolysed. Fig. 44.1 shows the reaction scheme of this process.

The whole reaction takes place in a working solution that consists of a mixture of various solvents (i.e. parts are aromatic solvents). The whole process is exothermic. In a second step, hydrogen peroxide is extracted from the working solution and concentrated. Within this study, both steps are included into the dataset together with the infrastructure and the transport amounts for the input materials.

44.3.2 Use of hydrogen peroxide

Due to its characteristics as a strong oxidising agent, hydrogen peroxide is widely used as a bleaching agent in the paper and the textile industry. Further important uses are e.g. wastewater treatment, disinfection applications or hydrometallurgical processes. In dilute solutions H_2O_2 acts as a very efficient antiseptic.

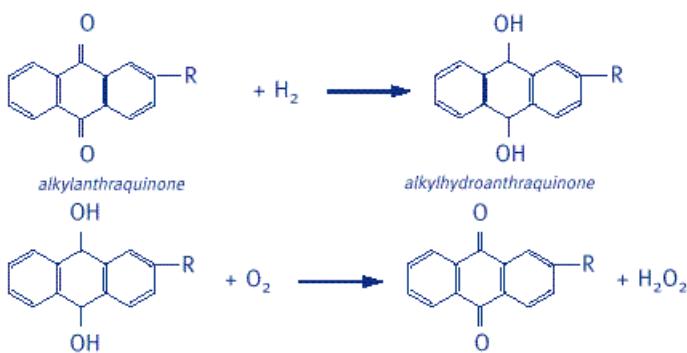


Fig. 44.1 Reaction scheme from the production of hydrogen peroxide by the anthraquinone process (from Boustead & Fawer (1998))

44.4 The anthraquinone production

Anthracinone ($C_{14}H_8O_2$, CAS-No. 84-65-1) is a solid with thin, light yellow needles. It is practically insoluble in water or in organic solvents. In the latter case, the solubility raises with increasing temperature. Anthraquinone exhibits thereby an extraordinary thermal stability – also together with oxidizing agents. The most important chemical and physical properties are summarized in Tab. 44.2.

Tab. 44.2 Chemical and physical properties of anthraquinone (Vogel (2000)).

Property	Value	Unit	Property	Value	Unit
Molecular weight	208.20	g mol ⁻¹	Melting point	287	°C
Density (at 25°C)	1.438	g cm ⁻³	Boiling point	377	°C

According to Vogel (2000), the production capacity for anthraquinone is about 34'000 t annually. Thereof, Western Europe produces about 50%, followed by Eastern Europe and Japan.

For the production four different production processes can be distinguished nowadays – with one of them accounting for almost 85% of the total production: oxidation of anthracene with chromic acid. The remaining 15% are produced by vapor-phase oxidation of anthracene with air, by naphthalene process or by synthesis from phthalic anhydride and benzene.

44.4.1 Process data

Main data source for this study is the information used at EMPA for the former inventories of hydrogen peroxide (Boustead & Fawer (1998); Dall'Acqua et al. (1999)), representing the last of the above mentioned production processes. Besides, information from Vogel (2000) about all four processes is used. Tab. 44.3 summarizes the information from Vogel (2000) – the respective information from EMPA is not shown here due to confidentiality reasons.

Tab. 44.3 Input and output data for the production of anthraquinone (information from Vogel (2000))

		chromic acid	oxidation with air	naphthalene	phthalic anhydride
Input					
water	kg	9000			
air (flow rate)	m ³ /h		2150	x	
anthracene	kg	2600	20 g/m ³		
sulphuric acid, 48%	kg	10200			
sodium dichromate, 20%	kg	23500			
naphthalene	kg			x	
xylene	kg			x	
butadiene	kg			x	
Output					
anthraquinone	kg	3000	x	x	

For this study, due to the fact that this second source allows no quantification of the process in three of the four cases, an average process from the chromic acid process in Tab. 44.3 and the information at EMPA from the former studies is established – with an amount of 80% chromic acid process. Therefore the following assumptions and approximations are used:

- **Material input:** It is assumed that the chromic acid process does not need any further substances than the ones mentioned in Tab. 44.3. The input of sulphuric acid and of sodium dichromate is expressed as amount of active substance only. As then the above listed amount of sulphuric acid is not sufficient for the process equation, instead the stoichiometric value based on an efficiency of 95% is used here. The amount of air consumed is not shown in the ecoinvent dataset according to Frischknecht et al. (2007). Three of the input materials (anthracene as well as chlorobenzene and aluminiumchloride from the information at EMPA) are not within the database ecoinvent. Therefore the following assumptions are used, based on information in Häussinger et al. (2000):
 - *Anthracene:* Produced by continuous distillation of tar coal, containing about 1.5% of anthracene - a process with several distillation and further purification steps. Therefore, the amount of anthracene used for the production of anthraquinone is shown in this study here as "chemical organics, unspecified".
 - *Chlorobenzene:* As chlorobenzenes are prepared industrially by reaction of liquid benzene with gaseous chlorine in the presence of a catalyst at moderate temperature and atmospheric pressure, in this study the amount of chlorobenzene is shown as benzene and chlorine, assuming a yield of 95%. Further environmental loads of the chlorbenzene production are not taken into account.
 - *Aluminiumchloride:* Today most anhydrous aluminium chloride is made by chlorinating aluminium, a highly exothermic reaction. Similar like for chlorobenzene, aluminium chloride is also shown here as pure aluminium and chlorine, again assuming a yield of 95%. Again, further loads are not taken into account.
- **Energy input:** In case of the chromic acid process no information about energy production is given. Therefore, it is assumed that the energy consumption is similar like in the other dataset. For the electricity consumed, an average European medium voltage mix (UCTE-mix) is used. The used steam is shown as "steam, for chemical processes, at plant (RER)" according to the description in Zah & Hischier (2007).
- **Infrastructure and Transport:** In the examined sources, no information about average transport distances for the raw materials used are indicated. Therefore, standard distances according to

Frischknecht et al. (2007) are used within this dataset. Concerning the infrastructure, due to a lack of more specific information, the module "chemical plant, organics (RER)" is used here.

- **Emissions to air and water:** The values for air emissions in the EMPA data indicated refer to process emissions. For the dust emissions, it is assumed in a conservative sense that they are 100% PM_{2,5}-emissions. In case of chromic acid process no such information is available. Thus, its emissions are estimated according to the following steps:
 - *Emissions to air:* 1% of the sulphuric acid input into the chromic acid process (as this is emitted easily into air) and 0.2% of the sodium dichromate input (assumption);
 - *Emission to water:* the remaining input (that means "total input" minus "stoechiometric amount for product" minus "air emissions"). Further it was assumed that all the waste water is treated in a internal waste water plant. No removal efficiency for sulphuric acid was assumed, leading to emissions of 220 g sulphuric acid per kg product in the treated water. The remaining amount of sodium dichromate is approximated by an emission of about 1 mol of sodium, e.g. 23 g/kg – and of 0.5 mol (due to a removal efficiency of 50%) of chromium ions, e.g. of 26 g/kg.

Due to confidentiality reasons, only the cumulated data from this dataset are available for the user of the database ecoinvent – the respective unit process is not accessible and therefore no table with data is shown here. Nevertheless, a uncertainty score is established according to the method used in this study (see Frischknecht et al. 2007) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. The data for one of the two production processes used is based on some few information from the literature, while the other part is the average from several producers. Accordingly the uncertainty is not so low, especially due to the fact that the producer data represents less than 20% of the established module. As the infrastructure and the transports of the input materials are based on very rough estimation, their respective uncertainty is high.

Nevertheless, the most important fields of the ecospold meta information from this dataset are listed in chapter 44.8.

44.5 The hydrogen peroxide production

44.5.1 Process data

Main data source is the information provided by eight hydrogen peroxide producer that has been the database used at EMPA for the former inventories of hydrogen peroxide (Boustead & Fawer (1998); Dall'Acqua et al. (1999)). As these data are confidential, they are not shown in details here in this study, but an average process is calculated of them and Tab. 44.4 shows this summarized process.

Tab. 44.4 Input and output data for hydrogen peroxide production (average value based on producer information)

Input		H2O2		Output		H2O2
<i>materials</i>				<i>product</i>		
hydrogen	m3	0.73		hydrogen peroxide	g	1000.00
aluminium oxide	g	9.61		waste		
quinone	g	0.64		waste to landfill	g	2.82
quinone & solvents	g	1.25		filter residues	g	4.43E-02
solvents, aromatic	g	0.99		waste, unspecified	g	88.74
solvents, unspecified	g	1.45		<i>emissions to air</i>		
sodium hydroxide	g	0.64		aromatic hydrocarbons	g	1.28E-01
inorganic chemicals	g	0.53		NMVOC	g	0.53
chemicals, unspecified	g	0.15		hydrogen	g	3.83E-02
air	g	214.95		Dust, particle	g	1.38E-04
nitrogen	g	50.84		<i>emissions to water</i>		
oxygen	g	29.33		BOD	g	0.26
water (process)	m3	1.92E-03		COD	g	0.94
water (cooling)	m3	0.17		TOC	g	0.30
<i>energy</i>				nitrate	g	2.03E-01
electricity	kWh	0.56		phosphate	g	1.25E-02
heavy fuel oil	g	6.16		suspended solids	g	1.51E-01
natural gas	m3	5.78E-02		chloride	g	0.38
steam	g	1581.89		hydrogen peroxide	g	0.60
				other emissions	g	3.75E-04

The inventory of hydrogen peroxide for this study is established, based on these data together with the following assumptions:

- **Material input:** Main raw material is hydrogen. For H₂ as well as the other input materials, the respective modules from the database ecoinvent are used. The input "quinone & solvents" is split according to the distribution of the other plants into 25% quinone and 75% solvents, aromatic type. This aromatic solvent amount is reported here as "benzene, at plant (RER)" due to the fact that this is one of the possibilities. The unspecified solvent amount is shown by the general module "solvent, unspecified, at plant (GLO)", described in the auxillaries chapter of the paper and board production (see Hischier (2007)). The amount of unspecified chemicals is integrated into the amount of "chemicals inorganic, at plant (GLO)". The amount of air consumed is not shown in the ecoinvent dataset according to Frischknecht et al. (2007).
- **Energy input:** For the electricity consumed, an average European medium voltage mix (UCTE-mxi) is used. Concerning the reported amounts of fuels (oil, gas) their respective industrial heating modules are used here, as no combustion emissions are reported. The used steam is shown as "steam, at plant (RER)" according to the description in Zah & Hischier (2007).
- **Infrastructure and Transport:** In the examined sources, no information about average transport distances for the raw materials used are indicated. Therefore, standard distances according to Frischknecht et al. (2007) are used within this dataset. Concerning the infrastructure, due to a lack of more specific information, the module "chemical plant, organics (RER)" is used here.
- **Emissions to air and water:** The values for air emissions indicated refer to process emissions. Therefore, it is not clearly understandable where the dust emissions from one of the producers are originating from. For this study, thus, this value is not taken into account. All other emissions are shown as reported. In accordance with the method, the electricity input is shown as waste heat output. Concerning the emissions to water, the value from "other emissions" is shown as "hydrocarbons, aromatic" (solvent emissions from one of the producers).

- Waste:** According to the information from several producers, the landfilled waste is mainly aluminium oxide from the process. In this study it is shown as “disposal, aluminium, 0% water, to sanitary landfill” due to a lack of more specific datasets. For the further wastes, as no information about the respective composition is given, the modules “disposal, residues from cooling tower, 30% water, to sanitary landfill” (filter residues) and “disposal, municipal solid waste, 22.9% water, to municipal incineration” (waste, unspecified) are used here.

44.5.2 Data quality considerations

The uncertainty scores established according to the method used in this study (see Frischknecht et al. (2007)) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. The data represent an average from several producers in Europe and have accordingly a quite small uncertainty. As the infrastructure and the transports of the input materials are based on very rough estimation, their respective uncertainty is much higher.

The resulting data together with their respective uncertainty values for the dataset „hydrogen peroxide, 50% in H₂O, at plant“ is shown in Tab. 58.4. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 44.8.

Tab. 44.5 In-/Outputs and uncertainty informations for the dataset "hydrogen peroxide, 50% in H₂O, at plant"

Explanation	Name	Location	Unit	hydrogen peroxide, 50% in H ₂ O, at plant	RER 0 kg	uncertainty Type	standardDeviation95%	GeneralComment	
								Location	InfrastructureProcess
								Unit	
Input from Technosphere	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	6.40E-04	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	hydrogen, liquid, at plant	RER	kg	6.56E-02	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	aluminium oxide, at plant	RER	kg	9.61E-03	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	anthraquinone, at plant	RER	kg	9.53E-04	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	benzene, at plant	RER	kg	1.93E-03	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	solvent, unspecified, at plant	GLO	kg	1.45E-03	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	nitrogen, liquid, at plant	RER	kg	5.08E-02	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	oxygen, liquid, at plant	RER	kg	2.93E-02	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	chemicals inorganic, at plant	GLO	kg	6.80E-04	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	5.60E-01	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	2.54E-01	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.10E+00	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	steam, for chemical processes, at plant	RER	kg	1.58E+00	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation		
	transport, freight, rail	RER	tkm	9.63E-02	1	2.09	(4,5,na,na,na,na); standard distances		
	transport, lorry 32t	RER	tkm	1.60E-02	1	2.09	(4,5,na,na,na,na); standard distances		
	disposal, residue from cooling tower, 30% water, to sanitary landfill	CH	kg	4.43E-05	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	disposal, aluminium, 0% water, to sanitary landfill	CH	kg	2.82E-03	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	disposal, municipal solid waste, 22.9% water, to municipal incineration	CH	kg	8.87E-02	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
Output Air emission	hydrogen peroxide, 50% in H ₂ O, at plant	RER	kg	1					
	Heat, waste		MJ	2.02E+00	1	1.13	(2,2,2,1,1,4); Average data from 8 European producers		
	Hydrocarbons, aromatic		kg	1.28E-04	1	2.02	(2,2,2,1,1,4); Average data from 8 European producers		
	NMVOCS, non-methane volatile organic compounds, unspecified origin		kg	5.30E-04	1	2.02	(2,2,2,1,1,4); Average data from 8 European producers		
	Hydrogen		kg	3.83E-05	1	1.52	(2,2,2,1,1,4); Average data from 8 European producers		
	BOD5, Biological Oxygen Demand		kg	2.60E-04	1	1.52	(2,2,2,1,1,4); Average data from 8 European producers		
	COD, Chemical Oxygen Demand		kg	9.40E-04	1	1.52	(2,2,2,1,1,4); Average data from 8 European producers		
	TOC, Total Organic Carbon		kg	3.00E-04	1	1.52	(2,2,2,1,1,4); Average data from 8 European producers		
	Suspended solids, unspecified		kg	1.51E-04	1	1.52	(2,2,2,1,1,4); Average data from 8 European producers		
	Nitrate		kg	2.03E-04	1	1.52	(2,2,2,1,1,4); Average data from 8 European producers		
Water emission	Phosphate		kg	1.25E-05	1	1.52	(2,2,2,1,1,4); Average data from 8 European producers		
	Chloride		kg	3.80E-04	1	1.52	(2,2,2,1,1,4); Average data from 8 European producers		
	Hydrogen peroxide		kg	6.00E-04	1	3.02	(2,2,2,1,1,4); Average data from 8 European producers		
	Hydrocarbons, aromatic		kg	3.75E-07	1	3.02	(2,2,2,1,1,4); Average data from 8 European producers		

44.6 Cumulative results and interpretation

Results of the cumulative inventory of both datasets can be downloaded from the database.

44.7 Conclusions

An average European dataset for the production of hydrogen peroxide, based on the information from various producers is established. For anthraquinone, average European data based on literature and two producers are established. Both datasets are in accordance with the present quality guidelines of the ecoinvent project. The data are thus of a good quality and can be used in a very broad context.

44.8 EcoSpold Meta Information

ReferenceFunction	Name	hydrogen peroxide, 50% in H ₂ O, at plant	anthraquinone, at plant
Geography	Location	RER	RER
ReferenceFunction	InfrastructureProcess	0	0
ReferenceFunction	Unit	kg	kg
ReferenceFunction	IncludedProcesses	This module contains material and energy input, production of waste and emissions for the production of hydrogen peroxide by the anthracinone process. Transport and infrastructure have been estimated. The input of 215 g air is not reported in the data according to the methodology of the study.	This module contains material and energy input, production of waste and emissions for the production of anthracinone. Transport and infrastructure have been estimated. The input of air is not reported in the data according to the methodology of the study.
ReferenceFunction	Amount	1	1
ReferenceFunction	LocalName	Wasserstoffperoxid, 50% in H ₂ O, ab Werk	Antrachinon, ab Werk
ReferenceFunction	Synonyms	dihydrogen dioxide//Hydroperoxide//Hioxy//Oxydol//Peroxan //peroxide	
ReferenceFunction	GeneralComment	data based on a study, performed by EMPA and Boustead Consulting, commissioned by CEFIC	data based on information from two producers and theoretical information from Ullmann's Encyclopaedy
ReferenceFunction	CASNumber	7722-84-1	84-65-1
TimePeriod	StartDate	1995	1995
TimePeriod	EndDate	1995	2000
TimePeriod	DataValidForEntirePeriod	1	1
TimePeriod	OtherPeriodText		
Geography	Text	average data from 8 European producers	data representing European conditions
Technology	Text	average technology used from these European producers	Average technology, representing a mix of 80% chromic acid process and the remaining 20% the synthesis out of phthalic anhydride and benzene.
Representativeness	Percent		
Representativeness	ProductionVolume		17'000 t
Representativeness	SamplingProcedure		The input of two of the "raw materials" is approximated by an input of the stoichiometric amounts needed for these raw materials, assuming a yield of 95%
Representativeness	Extrapolations	The amount of aromatic solvents is shown as "benzene".	
Representativeness	UncertaintyAdjustments		

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45 Iron(III) chloride

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Acknowledgement

Our thanks for the support for this specific inventory goes to R. Bitsch, M.Tyblewski; Solvay Zurzach / W.Bröll, Tessenderlo Schweiz / Aregger Chemie, Oensingen.

45.1 Introduction

Iron(III) chloride (FeCl_3 , CAS-No. 7705-08-0) is an almost black crystalline solid. Iron(III) chloride is very soluble in water. The solution is red to yellowish-brown, aqueous and odourless. Iron(III) chloride irritates the skin and especially eyes. The aqueous solution is strongly acidic (Ullmann 2001).

For this inventory the functional unit is 1 kg of iron(III) chloride (active substance). The inventory refers to a commercial aqueous solution with a concentration of 40 wt-% iron(III) chloride by weight. This equals an iron concentration of 14% by weight in the solution. Some chemical and physical properties of iron(III) chloride used in this inventory are given here.

Tab. 45.1 Chemical and physical properties of iron(III) chloride (Ullmann 2001)

Property	Unit	Value	Remarks
Molecular weight of anhydrous iron(III) chloride	g mol^{-1}	162.2	
Specific gravity of anhydrous iron(III) chloride	kg m^{-3}	2890	at 25 °C
Specific gravity of iron(III) chloride solution (40%)	kg m^{-3}	1430	at 20 °C
Enthalpy of solution of anhydrous iron(III) chloride	kJ mol^{-1}	95	formation of a 40 % solution at 20 °C

45.2 Reserves and Resources of material

Commercial production of iron(III) chloride solutions in Switzerland is mainly based on dissolving iron in hydrochloric acid and oxidizing the resulting iron(II) chloride with chlorine. In this process also spent pickling acid solutions containing iron(II) chloride are used as chlorine and iron source.

According to Ullmann 2001 in 1994 the production output (as 100% FeCl_3) in Europe was estimated to 150'000 t FeCl_3 per year. For Switzerland the consumption of 40% iron(III) chloride solution will account for about 20-25'000 t per year which equals 8-10'000 t FeCl_3 (100%) per year.

45.3 Use of material / product

Commercial forms of iron(III) chloride include sublimed anhydrous iron(III) chloride (99% FeCl_3), iron(III) chloride hexahydrate (ca. 60% FeCl_3), and iron(III) chloride solution (ca. 40% FeCl_3). The major commercial form is a solution with 40 wt-% FeCl_3 . For this inventory only the 40% iron(III) chloride solution was investigated. It was assumed that the main supply for Switzerland is produced within Switzerland and therefore imports were neglected.

The largest use of iron(III) chloride (around 90%) is in the form of dilute solutions that are employed as flocculating and precipitating agents in water treatment. According to data from the U.S. municipal wastewater treatment accounts for 59%, municipal potable water treatment for 22% and industrial water treatment for 8% of the consumption. Further uses of iron(III) chloride (11%) include electronic

and photographic etchants, metal surface treatment, catalysts and uses as a chlorinating and oxidising agent (ChemExpo 2000).

45.4 Systems characterization

The production of iron(III) chloride solutions was assessed using a production mix of the two main production processes applied in Switzerland. The process chain was assessed as shown here.

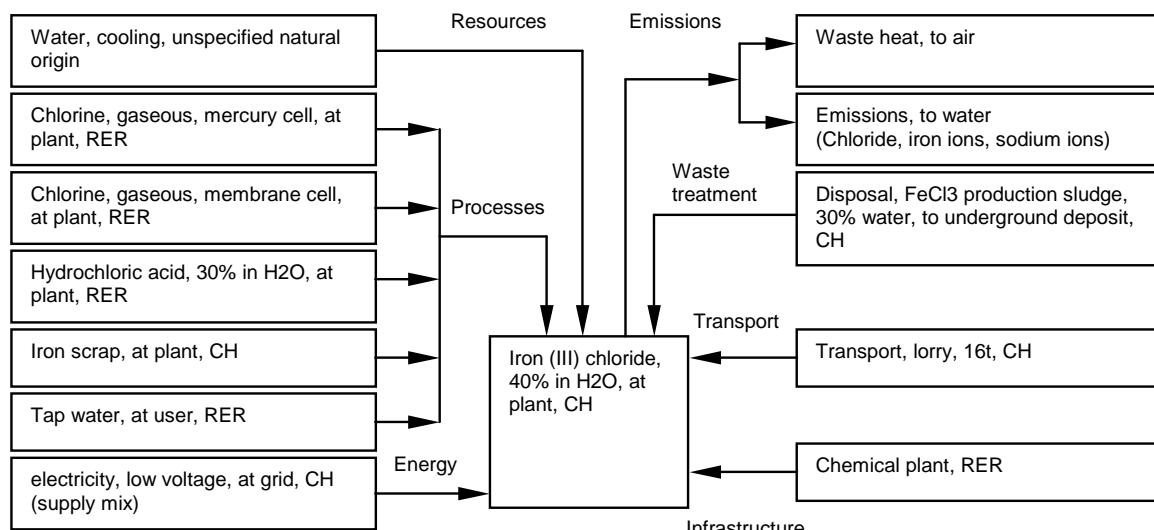


Fig. 45.1 Process chain for the production of Iron(III) chloride

The production processes used for chlorine production were chosen according to the actual share of the chlorine production used for iron(III) chloride production in Switzerland. For the inputs, scrap iron and the spent pickling bath⁵, only burdens for the transport from the producer to the plant and for scrap separation is included. As output only iron(III) chloride solution was concerned. Excess chlorine leaving the process can be further used within sodium hypochlorite production and was therefore not accounted as emission. As waste, the production process produces sludge containing water, carbon and metals. This sludge is disposed of in an underground deposit in Germany. As the production energy, only electricity was considered. Due to the exothermic reaction it was assumed that no further energy (fuel for heat and steam) is needed for the production process. There were no credits given for possibly available surplus steam from the reaction. Direct emissions from the process are chloride and iron emissions to water. There were no direct emissions to the soil considered.

45.5 Iron(III) chloride, 40% in H₂O, at plant

45.5.1 Process

Iron(III) chloride solutions are prepared by dissolving iron in hydrochloric acid and oxidizing the resulting iron(II) chloride with chlorine. In a continuous, closed-cycle process, iron(III) chloride solution is reduced with iron and the resulting iron(II) chloride solution is reoxidized with chlorine (Ullmann

⁵ Pickling bath, a solution of FeCl₂ and HCl, obtained as waste of the pickling process in steel processing industries. The pickling process is needed to remove the oxide layer that adheres to the steel surface. For this treatment often hydrochloric acid is used. According to the cut-off methodology of this project no emissions or resources were accounted for the production of the pickling bath because it was regarded as a waste product of the steel processing industry.

2001). In about 80% of the iron(III) chloride production in Switzerland, spent pickling acids are used as additional iron source. In average 92% of the iron used for iron(III) chloride production in Switzerland originates from iron scrap and only about 8% has pickling acid as iron source. Only few process data were available for the production of iron(III) chloride operating without pickling acid use. Therefore the same emissions and wastes were applied as for the process using pickling acids. The data presented in this inventory represent an average production process for iron(III) chloride in Switzerland. A simplified process scheme of iron(III) chloride production is shown here.

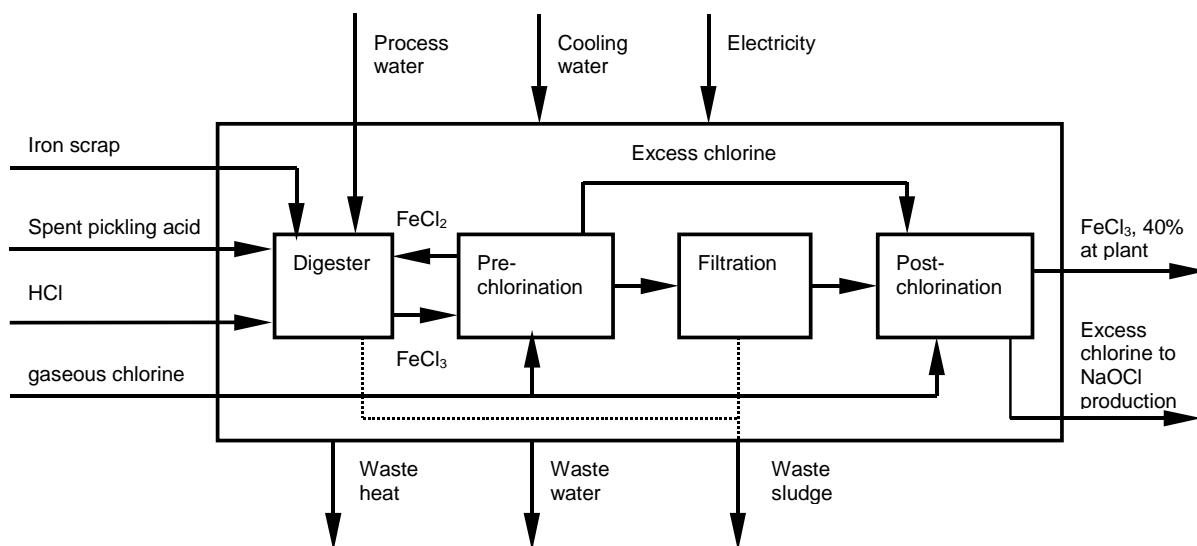


Fig. 45.2 Simplified process of iron(III) chloride production

The data for the process resources and emissions presented in the following chapters were derived from personal communications of two iron(III) chloride producers^{6,7}. For the average process for Switzerland presented in this inventory the data was combined and compared with data from iron(III) chloride production from iron ore presented in Bengtsson et al. 1997. From the process and emission data a process efficiency of 99.9% for chlorine and of 99.5% for iron (as 100% Fe) was determined. These process efficiencies were also used to check the raw material demand used in this inventory. A summary of the values used is given in Tab. 45.2.

45.5.2 Resources

Iron sources

As iron source mainly scrap iron or steel production wastes are used in Switzerland. To produce 1 kg iron(III) chloride, in average 0.328 kg scrap iron or steel production wastes are used. For this mostly low alloyed or construction steel, an iron content of 97.5% was assumed. This assumption leads to an amount of 0.320 kg Fe per kg FeCl₃ used for production. Further iron is derived from spent pickling acids containing HCl, FeCl₂ and FeCl₃. For this inventory an amount of 0.0261 kg Fe per kg FeCl₃ from pickling acids was applied. This iron originates from 0.3 kg pickling acid solution used per kg FeCl₃ produced. The total iron demand (as 100% Fe) amounts so to 0.346 kg Fe per kg FeCl₃.

⁶ Reply on questionnaire to iron(III) chloride production; Solvay AG, Zurzach; received 29. April 2002.

⁷ Personal communication; Aregger Chemie AG, Oensingen; March 2002.

Chlorine sources

As chlorine source gaseous chlorine is used. For this inventory it was assumed that the chlorine used for the process is separated before liquefaction step. Therefore, in contrary to liquid chlorine, the energy demand for liquefaction (0.07 kWh electricity per kg Cl₂) is not needed. For the delivery of the gaseous chlorine from the chlorine production plant nearby no transports are required (only a short pipeline). To produce 1 kg iron(III) chloride, in average 0.598 kg chlorine is needed. Further chlorine is derived from spent pickling acids and hydrochloric acid (0.3 kg pickling acid solution per kg FeCl₃). For this inventory an amount of 0.037 kg Cl per kg FeCl₃ from FeCl₂ and FeCl₃ in pickling acids and 0.022 kg Cl per kg FeCl₃ from hydrochloric acid was applied. This leads to a total chlorine demand of 0.657 kg Cl per kg FeCl₃.

For 80% of the chlorine the process “chlorine, gaseous, mercury cell, at plant, RER” was applied and for 20% of the chlorine the process “chlorine, gaseous, membrane cell, at plant, RER“ in order to assess an average chlorine production process in Switzerland relevant for iron(III) chloride production.

Process energy, electricity

There is only little electricity needed for mixing within the production process. According to Bengtsson et al. 1997 0.0236 kWh per kg FeCl₃ is needed. According to the data of the producer questioned the amount of electricity amounts for 0.0146-0.016 kWh per kg FeCl₃. This value seems low for a total electricity demand for the whole production process. For this inventory an average amount of 0.0186 kWh per kg iron(III) chloride produced was used (average of all values given). For the electricity the supply mix “electricity, medium voltage, at grid, CH” was used.

Process energy, heat

Because of the exothermic reaction no further heat (or steam) is needed according to the producer contacted. Some of the reaction heat is used for preheating the iron and for building heating. According to Bengtsson et al. 1997 0.006 MJ steam per kg FeCl₃ and 0.0198 MJ diesel fuel per kg FeCl₃ is needed. It remains unclear for what process the diesel fuel is needed. Due to the exothermic reaction no additional energy demand for steam production or room heating of the building was considered in this inventory. Because for the 40% iron(III) chloride solution no drying step is needed no further fuel demand for process operation was included in this inventory.

Water resources for process- and cooling-water

For the production of iron(III) chloride of a commercial grade with 40% FeCl₃, tap water or plant internal ground water is used as process water. For the production of 1 kg iron(III) chloride as a 40% solution, 1.5 kg water are needed. Due to the water content of the pickling acids, less water for processing is needed. According to the data of the producers an average process water consumption of 1.23 kg per kg FeCl₃ was calculated for this inventory. For this process water consumption the process “Tap water, at user, RER” was used.

Further water is needed for process cooling. The cooling water origins from river water or also from wells. From a total water demand (processing and cooling) of 7 kg per kg FeCl₃⁸, a cooling water demand of 5.77 kg per kg FeCl₃ was calculated (total water demand - process water). There were no data on treatment processes available for this water. Possible treatments of the cooling water with chemicals against fouling and scaling were neglected in this inventory.

⁸ Reply on questionnaire to iron(III) chloride production; Solvay AG, Zurzach; received 29. April 2002.

Treatment chemicals

There is no demand of additional treatment chemicals within the process.

Used processes

For the electricity demand the supply mix “electricity, medium voltage, at grid, CH” was used. For chlorine production the processes “chlorine, gaseous, mercury cell, at plant, RER” and “chlorine, gaseous, membrane cell, at plant, RER“ were used. For the scrap iron used the process “iron scrap, at plant, CH“ was applied. For the pickling acid solutions no production process was applied, because those solutions were considered as wastes of galvanic industries and therefore bear no burden for production. For further hydrochloric acid the process “hydrochloric acid, 30% in H₂O, at plant, RER“ was applied. For these solutions only transport requirements were considered. A summary of the values used is given in the following table.

Tab. 45.2 Iron(III) chloride production. Energy and resource demands.

Resource, Use	Unit	per kg FeCl ₃	per kg 40% FeCl ₃ solution
Water, cooling, unspecified natural origin	m ³	5.77 * 10 ⁻³	2.31 * 10 ⁻³
Tap water, at user, for processing	kg	1.23	0.492
Chlorine, gaseous, mercury cell production	kg	0.492	0.197
Chlorine, gaseous, membrane cell production	kg	0.106	0.0424
Iron scrap, at plant	kg	0.328	0.131
hydrochloric acid, 30% in H ₂ O, at plant	kg	0.022	0.009
Pickling acid solution (with 21-33% H ₂ O) ¹	kg	0.3	0.12
Electricity, medium voltage, for processing ²	kWh	18.6 * 10 ⁻³	7.44 * 10 ⁻³

¹ Not considered as a resource process (waste of metal pickling processes).

² Supply mix for Switzerland.

45.5.3 Emissions

Emissions to air

According to Bengtsson et al. 1997 0.16 * 10⁻⁶ kg Cl₂ per kg FeCl₃ are emitted during production. Within the considered plant this excess chlorine can be used for the processing of sodium hypochlorite. Therefore there were no chlorine emissions accounted. The amount of chlorine emission is small due to the use of scrubbers for emission control. There were no other emissions to air reported.

Waste heat.

The waste heat from the exothermic process influences the total process energy demand. From this waste heat also some heat is used for preheating and building heating processes. Because in this project no waste heat of chemical reaction is concerned within the reaction process, the waste heat produced in the iron(III) chloride production is not considered here.

The waste heat of the used electricity has to be considered here. It was assumed, that 100% of the electricity consumed is converted to waste heat, which dissipates to the air (e.g. from motors). The calculated value for this waste heat is 0.067 MJ per kg FeCl₃ produced.

Tab. 45.3 Iron(III) chloride production. Emissions to air.

Emission	Unit	per kg FeCl ₃	per kg 40% FeCl ₃ solution
Waste heat to air ¹	MJ	67 * 10 ⁻³	26.8 * 10 ⁻³

¹ Only waste heat from electricity use considered. Waste heat from reaction in preceding processes considered.

Emissions to Water

As emissions to water chloride and iron ions were considered. For this inventory as emissions to water an amount of $0.5 * 10^{-3}$ kg chloride and $0.25 * 10^{-3}$ kg iron ions per kg FeCl₃ was applied⁹. The sodium emissions to water were calculated of the applied amount of sodium hydroxide for scrubbing. It was assumed, that this emissions were released to a river. There was no data on further process emissions to water available and considered. In Tab. 45.4 a summary of the values used is given.

Tab. 45.4 Iron(III) chloride production. Emissions to water.

Emission	Unit	per kg FeCl ₃	per kg 40% FeCl ₃ solution
Chloride (Cl ⁻), to river	kg	$200 * 10^{-6}$	$80 * 10^{-6}$
Iron ion (Fe ⁺⁺), to river	kg	$100 * 10^{-6}$	$40 * 10^{-6}$

45.5.4 Wastes and emissions to soil

The production process produces sludge due to impurities in the scrap iron and the pickling acids. This sludge has a high content of water, carbon and metals. Most of this sludge is disposed of in an underground deposit in Germany. According to the producers the amount of sludge to dispose accounts from 0.001 kg to 0.006 kg sludge per kg FeCl₃. In Bengtsson et al. 1997 a much higher value of 0.015 kg sludge per kg FeCl₃ is given. For this inventory a value of 0.006 kg sludge per kg FeCl₃ was used⁹. An overview of the typical elemental composition of this sludge is given in Tab. 45.5. There was no data on further process wastes and emissions to soil available and considered.

⁹ Reply on questionnaire to iron(III) chloride production; Solvay AG, Zurzach; received 29. April 2002.

Tab. 45.5 Iron(III) chloride production. Composition of waste sludge

Element	Share in %	Unit	per kg FeCl₃	per kg 40% FeCl₃ solution
Total amount of sludge	100%	kg	6.0E-03	2.4E-03
Water (H ₂ O)	ca. 30%	kg	1.8E-03	7.2E-04
Oxygen ¹	27.60%	kg	1.7E-03	6.6E-04
Carbon, as graphite	20.00%	kg	1.2E-03	4.8E-04
Iron ²	7.70%	kg	4.6E-04	1.8E-04
Silicium	11.70%	kg	7.0E-04	2.8E-04
Sulphur	2.00%	kg	1.2E-04	4.8E-05
Phosphorus	0.40%	kg	2.4E-05	9.6E-06
Chromium	0.50%	kg	3.0E-05	1.2E-05
Molybdenum	0.10%	kg	6.0E-06	2.4E-06
Nickel	0.05%	kg	3.0E-06	1.2E-06
Copper	0.01%	kg	6.0E-07	2.4E-07
Zinc	0.01%	kg	6.0E-07	2.4E-07
Lead	0.01%	kg	6.0E-07	2.4E-07
Cadmium	0.0050%	kg	3.0E-07	1.2E-07
Cobalt	0.0010%	kg	6.0E-08	2.4E-08
Mercury	0.0002%	kg	1.2E-08	4.8E-09

¹ Oxygen contained in metal oxides (mainly Fe₂O₃) and SiO₂.

² Non-specified metal oxides accounted as iron oxides (Fe₂O₃)

45.5.5 Infrastructure and transport processes

Infrastructure and land use

The land use is already included in the infrastructure process of the production facility and therefore not considered separately. There was no data of the specific infrastructure of the average iron(III) chloride production available. Therefore the infrastructure of the production facility, containing the buildings and the equipment, was approximated with data for an average chemical plant. This infrastructure for chemical production was assessed with a plant complex with an output of 50 kt a⁻¹ of various chemical products. The lifetime of the whole site was assumed to be 50 years. Therefore the infrastructure has to be divided by a production of 2.5 Mt. As product the iron(III) chloride solution containing 40% FeCl₃ was considered. With this product output an infrastructure value of 0.4 * 10⁻⁹ units per kg iron(III) chloride solution or 1 * 10⁻⁹ units per kg FeCl₃ was calculated (see Tab. 45.6).

Transport processes

The only materials needed in the process where additional transportation has to be considered are the iron scrap and the pickling acids. The iron scrap and pickling acid used for the production origins from companies nearby the plant. The transportation distance was therefore estimated to be around 30 km. This transport is carried out mainly by lorry. For the transport of the sludge to the underground deposit a distance of 500 km road transport (lorry 16t) was used. In total an amount of 0.022 tkm per kg FeCl₃ for lorry transports (lorry 16t) was used in this inventory. For the chlorine used in the production proc-

ess and the additional hydrochloric acid used no transports were considered because those chemicals are produced in the chlorine plant nearby (e.g. delivered by pipeline). The calculated transport requirements are listed in Tab. 45.6.

For delivering the iron(III) chloride solutions to the customer, rail transport is used to a large extend (Chem-oil-online 2001). Due to the high water content of the product, delivery distances are normally smaller than 200 km. The transport to the customer (e.g. a waste water treatment plant) is not included in this inventory, because the system border of this process is the gate of the production plant.

Tab. 45.6 Iron(III) chloride production. Infrastructure and transport processes

Land use	Unit	per kg FeCl ₃	per kg 40% FeCl ₃ solution
Chemical plant ¹	unit	1 * 10 ⁻⁹	0.4 * 10 ⁻⁹
Transport, lorry, 16t ²	tkm	0.022	0.009

¹ Infrastructure approximated with data for average chemical production. The production output of the chemical plant was related to the production output iron(III) chloride solution with 40 wt-% water content.

² 30 km transport for scrap iron and pickling acids. 500 km transport for waste sludge to underground deposit.

45.6 Data quality considerations

The following table shows the data quality indicators for the inventory of iron(III) chloride production in Switzerland. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. The highest uncertainties exist for the emission data due to variations of the source materials. Also the data for energy use contains uncertainties because no complete energy balance of the plants was available. In general the infrastructure data has a high uncertainty: Because of missing specific data an approximation with an average chemical production plant was used.

Tab. 45.7 In- / Outputs for the module “Iron (III) chloride, 40% in H₂O, at plant”, location CH

Process output: 1 kg, iron (III) chloride, 40% in H ₂ O, at plant, CH	Name, Location	Value	Unit	Uncertainty			Comment
				Type	Score	St.Dev.	
From technosphere	chlorine, gaseous, mercury cell, at plant, RER	4.92E-1	kg	lognorm	3,2,1,3,1,5	1.24	Calculated from data of producer. Location RER
	chlorine, gaseous, membrane cell, at plant, RER	1.06E-1	kg	lognorm	3,2,1,3,1,5	1.24	Calculated from data of producer. Location RER
	iron scrap, at plant, RER	3.28E-1	kg	lognorm	3,2,1,1,1,5	1.24	Calculated average from data of producer
	hydrochloric acid, 30% in H ₂ O, at plant, RER	2.20E-2	kg	lognorm	4,2,1,3,4,5	1.62	Value calculated from stoichiometry. Location RER
	tap water, at user, RER	1.23E+0	kg	lognorm	3,2,1,3,3,5	1.32	Calculated from data of producer, assumptions
	electricity, medium voltage, at grid, CH	1.86E-2	kWh	lognorm	3,4,1,3,1,5	1.26	Calculated average from mixed data
	transport, lorry 16t, CH	2.20E-2	tkm	lognorm	4,2,1,1,3,5	2.14	Value calculated with assumed distances
	disposal, sludge from FeCl ₃ production, 30% water, to underground deposit, DE	6.00E-3	kg	lognorm	3,2,1,1,3,5	1.32	Data from 1 major producer
	chemical plant, organics, RER	1.00E-9	unit	lognorm	5,5,1,3,4,5	3.55	Estimated value. Proxy process used
⇒	Water, cooling, unspecified natural origin	5.77E-3	m ³	lognorm	3,2,1,1,3,5	1.32	Calculated average from data of producer
	Heat, waste, to air, low population density	6.70E-2	MJ	lognorm	3,2,1,1,1,5	1.24	Calculated from Electricity demand
✉	Chloride, to water, river	2.00E-4	kg	lognorm	3,2,1,1,3,5	1.63	Data of 1 major producer, unknown sample size
	Iron, ion, to water, river	1.00E-4	kg	lognorm	3,2,1,1,3,5	1.63	Data of 1 major producer, unknown sample size

(1) Resources, (2) Emissions

45.7 Cumulative results and interpretation

Results of the cumulative inventory of both datasets can be downloaded from the database.

45.8 Conclusions

The production of iron(III) chloride is determined largely by the impact of the chlorine used. Because the iron used in the production originates from scrap or waste pickling acids, the impact to the total bur-

den is small. The required process energy is also small due to the exothermic reaction of the process. There are uncertainties within the data of the emissions and probably also concerning some emissions not considered in this work. In future work on this inventory, the process emissions (especially to water) should be investigated further.

45.9 References

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46 Iron-nickel-chromium alloy

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Last changes:

10.12.2007

46.1 Introduction

Many applications in the chemical and petrochemical industry as well as power plants and gas-turbine components need alloys with high corrosion resistance, high-temperature and oxidation resistance. In such applications, iron-nickel-chromium alloys can lead to better performance or longer service life and are therefore used despite their high cost.

46.2 Characterisation of material product

Thousands of different alloys contain nickel or chrome, each of them developed to offer a particular combination of technical properties (corrosion resistance, mechanical properties and service life) relevant to specific conditions of use. Stainless steel commonly has a nickel content of 8-14 percent, rising to 15-40 percent in special engineering alloys and 40-90 percent in special alloys for the aerospace and electronic industries.

Tab. 46.1 shows the principal composition of various iron-nickel-chromium alloys similar to the one modelled in this inventory.

Tab. 46.1 Composition used in the inventory and iron-nickel-chromium alloys with similar composition

Brand Name	Material Number	Nickel %	Iron %	Chromium %	Molybdenum %
Incoloy 800, 800H, 800HT	1.4876, 1.4958, 1.4959 UNS N08800, N08810, N08811	30-35	39.5 min.	19-23	
Incoloy 803	UNS S35045	32-37	Balance	25-29	
Incoloy 825	2.4858, UNS N08825	38-46	22 min.	19.5-23.5	2.5-3.5
Incoloy 864	UNS S35135	30-38	Balance	20-25	4.0-4.8
Incoloy Alloy 020	UNS N08020	32-38	Balance	19-21	2.0-3.0
Inconel 706	UNS N09706	39-44	Balance	14.5-17.5	
Used in this Inventory		32	Balance	21	

46.3 Reserves and resources of material

It is common practice for special alloys to be recycled from identical scrap wherever possible. In practice, it is often not possible to segregate products and scrap into specific alloys. Alloys and products get mixed. Apart from the possibility of re-melting scrap mixtures in order to produce ingots of known composition, it is feasible to adjust the composition of the scrap by adding controlled amounts of primary metals in order to produce ingots of the required specification. For the process modelled here, it is assumed that primary metals (nickel, chromium) are added to the scrap.

46.4 Use / application of product

Nickel-iron-chromium alloys such as Incoloy 800 H and Incoloy 803 have high strength and excellent resistance to oxidation and carburisation in high-temperature atmospheres. They are used in chemical and petrochemical processing plants, in super-heaters for power plants and industrial furnaces. Other alloys (such as Incoloy 825 or Alloy 020) are particularly resistant to sulphuric and phosphoric acids.

Such alloys are used in acid production and pickling equipment, pollution-control equipment as well as in nuclear fuel reprocessing (SMC, 2001).

46.5 System characterisation

The alloying processes of iron-nickel-chromium alloys include electric-arc, air-induction and vacuum-induction melting. This process is approximated with the process “steel, electric, chromium steel 18/8, at plant” as described in Classen et al. (2007).

46.6 Iron-nickel-chromium alloy, at plant

46.6.1 Process

The production of iron-nickel-chromium alloy is modelled with the process of electric-arc furnace production to produce 18/8 chromium steel (Classen et al., 2007). This process uses secondary steel. The scrap is used only as iron-bearing input. The chromium input is also modelled as ferrochromium input (high-carbon ferrochromium with 68% Cr and 4-10% C). Ferronickel (25% Ni) cannot be used for this alloy because of its high nickel content. The nickel input is modelled with class I nickel (99.5% Ni). Iron scrap is used as main iron input. A surplus of 10.5% metal input is used in analogy to the stainless steel process described in (Classen et al., 2007). The metal input used for iron-nickel-chromium alloy production in an electric arc furnace is shown in Tab. 46.2.

Tab. 46.2 Metal input for 18/8 chromium steel and iron-nickel-chromium alloy production in an electric arc furnace

Input material	Unit	Steel, electric, chromium steel 18/8, at plant ¹	Iron-nickel-chromium alloy, at plant
		kg	kg
Iron scrap	kg	0.52	0.474
Ferrochromium, high-carbon, 68% Cr	kg	0.265	0.309
Ferronickel, 25% Ni	kg	0.32	0
Nickel, 99.5%	kg	0	0.322
Total Input (110.5% of Output)	kg	1.105	1.105

¹ Production process as described in Classen et al. (2007)

46.6.2 Energy use, emissions and infrastructure

An identical process energy, process emission and infrastructure requirement to that used in the process “steel, electric, chromium steel 18/8, at plant” (Classen et al., 2007) is assumed.

46.6.3 Data quality considerations

Tab. 46.3 shows the unit process raw data and data-quality indicators of the inventory of iron-nickel-chromium alloy, at plant.

A simplified approach with a pedigree matrix is used to calculate the standard deviation. However, the basic uncertainty is adjusted to represent the ranges of the data obtained from a study of the literature for carbon steel and stainless steel. The inventory uses a production process for stainless steel, so that large uncertainties occur due to different possible process emissions and energy use. Further uncertainties are due to the unknown nickel content in the recycled scrap and therefore also in the nickel input.

Tab. 46.3 Unit process raw data of iron-nickel-chromium alloy, at plant

product	Name Location InfrastructureProcess Unit	Location InfrastructureProcess Unit	RER 0 kg	iron-nickel- chromium alloy, at plant	UncertaintyType	StandardDeviation9 5%	GeneralComment
technosphere	iron-nickel-chromium alloy, at plant	RER 0 kg	1				
	oxygen, liquid, at plant	RER 0 kg	5.07E-2	1	1.52	(2,3,2,3,4,3); see remark	
	quicklime, in pieces, loose, at plant	CH 0 kg	5.50E-2	1	1.52	(2,3,2,3,4,3); see remark	
	refractory, basic, packed, at plant	DE 0 kg	1.35E-2	1	1.52	(2,3,2,3,4,3); see remark	
	electricity, medium voltage, production UCTE, at grid	UCTE 0 kWh	4.25E-1	1	1.52	(2,3,2,3,4,3); see remark	
	hard coal mix, at regional storage	UCTE 0 kg	1.40E-2	1	1.52	(2,3,2,3,4,3); see remark	
	anode, aluminium electrolysis	RER 0 kg	3.00E-3	1	1.52	(2,3,2,3,4,3); see remark	
	electric arc furnace converter	RER 1 unit	4.00E-11	1	3.45	(5,nA,nA,nA,4,nA); see remark	
	iron scrap, at plant	RER 0 kg	4.74E-1	1	1.56	(4,nA,nA,nA,4,nA); iron input from scrap, balance to 110.5% of output	
	natural gas, high pressure, at consumer	RER 0 MJ	9.75E-1	1	1.52	(2,3,2,3,4,3); see remark	
	transport, lorry >16t, fleet average	RER 0 tkm	9.28E-1	1	2.24	(5,4,nA,nA,nA,nA); see remark	
	transport, freight, rail	RER 0 tkm	9.29E-1	1	2.24	(5,4,nA,nA,nA,nA); see remark	
	disposal, inert waste, 5% water, to inert material landfill	CH 0 kg	5.00E-3	1	1.52	(2,3,2,3,4,3); see remark	
	disposal, slag, unalloyed electr. steel, 0% water, to residual material landfill	CH 0 kg	7.68E-2	1	1.52	(2,3,2,3,4,3); see remark	
	ferrochromium, high-carbon, 68% Cr, at plant	GLO 0 kg	3.09E-1	1	1.56	(4,nA,nA,nA,4,nA); share of Cr in scrap input not known	
	nickel, 99.5%, at plant	GLO 0 kg	3.22E-1	1	1.56	(4,nA,nA,nA,4,nA); share of Ni in scrap input not known	
	disposal, dust, alloyed EAF steel, 15.4% water, to residual material landfill	CH 0 kg	5.10E-3	1	1.52	(2,3,2,3,4,3); see remark	
emission air, unspecified	Benzene	- - kg	2.28E-6	1	1.79	(2,3,2,3,4,3); see remark	
	Benzene, hexachloro-	- - kg	2.00E-8	1	3.24	(2,3,2,3,4,3); see remark	
	Cadmium	- - kg	3.65E-8	1	5.27	(2,3,2,3,4,3); see remark	
	Carbon monoxide, fossil	- - kg	2.32E-3	1	5.27	(2,3,2,3,4,3); see remark	
	Chromium	- - kg	1.25E-6	1	5.27	(2,3,2,3,4,3); see remark	
	Copper	- - kg	2.30E-7	1	5.27	(2,3,2,3,4,3); see remark	
	Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin	- - kg	4.54E-12	1	3.24	(2,3,2,3,4,3); see remark	
	Heat, waste	- - MJ	3.04E+0	1	1.52	(2,3,2,3,4,3); see remark	
	Hydrocarbons, aromatic	- - kg	7.70E-5	1	1.79	(2,3,2,3,4,3); see remark	
	Hydrogen chloride	- - kg	5.20E-6	1	1.79	(2,3,2,3,4,3); see remark	
	Hydrogen fluoride	- - kg	2.35E-6	1	1.79	(2,3,2,3,4,3); see remark	
	Lead	- - kg	1.81E-6	1	5.27	(2,3,2,3,4,3); see remark	
	Mercury	- - kg	2.24E-6	1	5.27	(2,3,2,3,4,3); see remark	
	Nickel	- - kg	7.00E-7	1	5.27	(2,3,2,3,4,3); see remark	
	Nitrogen oxides	- - kg	1.80E-4	1	1.79	(2,3,2,3,4,3); see remark	
	PAH, polycyclic aromatic hydrocarbons	- - kg	3.72E-8	1	3.24	(2,3,2,3,4,3); see remark	
	Particulates, < 2.5 um	- - kg	1.66E-4	1	3.24	(2,3,2,3,4,3); see remark	
	Particulates, > 10 um	- - kg	5.86E-5	1	1.79	(2,3,2,3,4,3); see remark	
	Particulates, > 2.5 um, and < 10um	- - kg	1.66E-4	1	2.24	(2,3,2,3,4,3); see remark	
	Polychlorinated biphenyls	- - kg	2.32E-8	1	3.24	(2,3,2,3,4,3); see remark	
	Sulfur dioxide	- - kg	7.70E-5	1	1.52	(2,3,2,3,4,3); see remark	
	Zinc	- - kg	2.29E-5	1	5.27	(2,3,2,3,4,3); see remark	

Remark to general comment: Based on data from chromium steel production with electric arc furnace (EAF)

46.7 Cumulative results and interpretation

46.7.1 Introduction

Selected LCI results and values for the cumulative energy requirement are presented and discussed in this section. Please note that only a small part of the 1500 elementary flows is presented here. The selection of the elementary flows shown in the tables is not based on their environmental relevance. Rather, it allows the contributions of the different life cycle phases or specific inputs from the technosphere to the selected elementary flows to be illustrated. Please refer to the *ecoinvent* database for the complete LCIs.

The selection shown is unsuitable for a life-cycle assessment of the analysed processes and products. Please download data from the database for your own calculations, not least because of possible minor deviations between the presented results and the database due to corrections and changes made in the background data used as inputs to the relevant dataset.

The *ecoinvent* database also contains the results of life-cycle impact assessments. Assumptions and interpretations are necessary to match current LCIA methods to the *ecoinvent* inventory results. They are described in Frischknecht et al. (2007). You are strongly advised to read the respective sections of the implementation report before applying the LCIA results.

46.7.2 Selected LCI results

The major part of the carbon dioxide (76%), NMVOC (79%), nitrogen oxide emissions (79%), the cumulative energy demand (fossil: 73%, nuclear: 67%) and the land use (86%) are caused by the nickel demand. With 8-15% of the total emissions ferrochromium is also of importance. The electricity used is of importance for the cumulative energy demand (5-14%). Tab. 46.4 shows selected LCI results and cumulative energy demands for the process iron-nickel-chromium alloy, at plant.

Tab. 46.4 Selected LCI results and the cumulative energy demand for iron-nickel-chromium alloy, at plant

Ecocat	Ecosubcat	Name	Name	iron-nickel-chromium alloy, at plant
			Location Unit	RER kg
cumulative energy demand	fossil	non-renewable energy resources, fossil	MJ-Eq	5.56E+01
	nuclear	non-renewable energy resources, nuclear	MJ-Eq	1.31E+01
	primary forest	non-renewable energy resources, primary forest	MJ-Eq	1.35E-04
	water	renewable energy resources, water	MJ-Eq	1.50E+01
	biomass	renewable energy resources, biomass	MJ-Eq	9.57E-01
	wind	renewable energy resources, kinetic (in wind), converted	MJ-Eq	2.24E-01
	geothermal	renewable energy resources, geothermal, converted	MJ-Eq	0.00E+00
	solar	renewable energy resources, solar, converted	MJ-Eq	3.26E-03
	resource	land occupation	m2a	4.45E-01
selected LCI results	air	CO2, fossil	kg	4.49E+00
	air	NMVOC	kg	5.17E-03
	air	nitrogen oxides	kg	2.71E-02
	air	sulphur dioxide	kg	4.50E-01
	air	particulates, <2.5 um	kg	1.43E-02
	water	BOD	kg	1.30E-02
	soil	cadmium	kg	1.26E-09

46.8 Conclusions

Due to the high impact of the nickel alloy, the environmental impact is strongly dependent on the share of recycling material (scrap of identical composition) used. For the process modelled here, it is assumed that only iron bearing scrap is used and all the nickel- and chromium alloys are added.

46.9 Appendices: EcoSpold Meta Information

Tab. 46.5 EcoSpold Meta Information of iron-nickel-chromium alloy, at plant

ReferenceFunction	Name	iron-nickel-chromium alloy, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
DataSetInformation	Type	1
	Version	2.0
	energyValues	0
	LanguageCode	en
	LocalLanguageCode	de
DataEntryBy	Person	72
	QualityNetwork	1
ReferenceFunction	DataSetRelatesToProduct	1
	IncludedProcesses	Transports of scrap metal and other input materials to electric arc furnace, steel-making process and casting.
	Amount	1
	LocalName	Eisen-Nickel-Chrom-Legierung, ab Werk
	Synonyms	Incoloy 800//1.4876
	GeneralComment	Class I nickel as nickel input and ferrochromium (68% Cr) as chromium input used. Scrap is only used as iron bearing input. No nickel or chromium input from the iron scrap assumed.
	InfrastructureIncluded	1
	Category	metals
	SubCategory	extraction
	LocalCategory	Metalle
	LocalSubCategory	Gewinnung
	Formula	X10NiCrAlTi 32-20
	StatisticalClassification	
	CASNumber	
TimePeriod	StartDate	2000
	EndDate	2005
	DataValidForEntirePeriod	1
	OtherPeriodText	
Geography	Text	Data relate to EAF plants in the EU
Technology	Text	EAU-Process for stainless steel used as approximation for the production of high alloyed iron-nickel-chromium alloys. EU technology mix for electric arc furnace process (mainly furnace with 4th hole, partly with additional evacuation of building atmosphere).
Representativeness	Percent	
	ProductionVolume	unknown
	SamplingProcedure	based on literature
	Extrapolations	none
	UncertaintyAdjustments	none
DataGeneratorAndSource	Person	72
	DataPublishedIn	2
	ReferenceToPublishedSource	8
	Copyright	1
	AccessRestrictedTo	0
	CompanyCode	
	CountryCode	
	PageNumbers	Iron-nickel-chromium alloy
	Validator	42
	Details	automatic validation in Excel
ProofReading	OtherDetails	none

46.10 References

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47 Isopropanol

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 Review: Heiko Kunst, TU Berlin

47.1 Introduction

Isopropanol, also called 2-propanol (C_3H_7OH , CAS-No. 67-63-0) is a clear, colourless, flammable liquid with a slight odour. It is completely miscible with water and can be mixed with quite a lot of further solvents (e.g. ethers, acids, ketones or alcohols). The most important chemical and physical properties of water-free (anhydrous) isopropanol are given here (Papa (2000)).

Tab. 47.1 Chemical and physical properties of anhydrous isopropanol

Property	Value	Isopropanol	Remarks
Molecular weight	$g\ mol^{-1}$	60.096	
Vapor pressure	kPa	4.414	at 20 °C
Boiling point	°C	82.26	at normal pressure
Melting point	°C	-88.5	at normal pressure

47.2 Reserves and Resources of material

The annual worldwide production capacity in 1996 was about 1.9 Mt per year. Thereof, the United States and Western Europe (without Germany) have about similar parts (each about 0.75 Mt), while the remaining part is in Germany and in Japan. Since the production of acetone shifts more and more away from isopropanol as main raw material, and in the coatings more and more waterborne or high-solid substances are used, the production of isopropanol won't continue its growth of the last decades.

47.3 Use of material / product

Isopropanol is used mainly as a solvent in the ink production and the surfactant production. According to Papa (2000), there exists a quite long list of further applications for isopropanol – from the use as antiseptic alcohol until being itself the source for further organics synthesis. The consumption in the United States in 1990 of a total of 33 kt was distributed to coating solvents (28%), processing solvents (21%), household/personal use (16%), pharmaceuticals (16%), acetone production (11%) and further solvent applications. Similar information for Europe was not available.

47.4 Systems characterization

In the production process for isopropanol the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of isopropanol is not considered to be high.

According to Papa (2000), it has only two relevant reaction ways for the production of isopropanol: the indirect and the direct hydration of propene. No information about the importance of the two different production routes is available and therefore, for this study, a 50:50 split was assumed. The functional unit for the inventory is 1 kg of anhydrous isopropanol. As process location Europe (RER) is used.

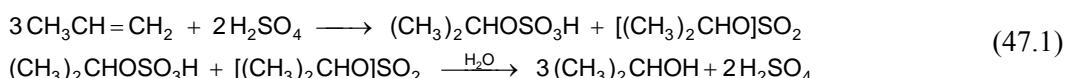
47.5 Isopropanol, at plant (Location: RER)

47.5.1 Process

This dataset includes a rough estimation of the production process of isopropanol by the indirect and the direct hydration of propene (50:50 split). Due to missing production data this inventory bases on information given in Papa (2000). The emissions to air and water were estimated using mass balance. It was assumed that wastewater is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is quite large.

Indirect Hydration

This production scheme involves two production steps - in the first one, propene and sulphuric acid are reacted together, resulting in a mixture of mono- and diisopropyl sulphate esters. In the second step, these esters are hydrolyzed for the production of isopropanol. The overall reaction can be formulated as follows:



For this indirect hydration reaction weak or strong acid can be used. The flow scheme of a weak acid production plant is shown in the figure below. While in this process a 60% acid solution is used at about 75-85°C and 0.6-1 MPa, the strong-acid process uses a >90% acid solution at 20-30°C and 1-1.2 MPa.

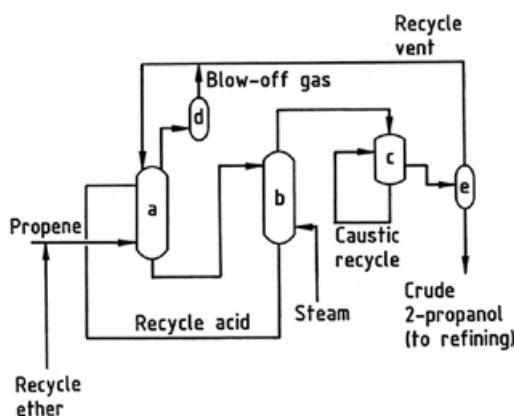


Fig. 47.1 Flow sheet for the production of isopropanol by indirect, weak-acid process: a) absorbers; b) strippers; c) caustic scrubber; d) (Fig. 2 out of Papa (2000))

Main advantage of the weak-acid process is the fact that this process can use low-purity propene feed. On the other hand side, this process has high corrosion rates and several disposal problems for its different wastes and effluents. The strong-acid process has no commercial importance - mainly due to the fact that this process requires high-purity propene feed and has similar disposal problems like the weak-acid process.

Direct Hydration

According to Papa (2000), this production type exists since the beginning of the 50s. Its overall reaction can be formulated as follows:



Main characteristics for this process are high pressure and low temperature over a acidic fixed-bed catalyst. Across the world, three different types of such a direct hydration process exist (more details, see Papa (2000)). In Europe mainly the so-called "phosphoric acid" process is used. Here, a phosphoric acid catalyst supported on SiO_2 is operated at 180-260°C and a pressure of 2.5-6.5 MPa.

47.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the wastewater treatment. Fossil fuel is needed to generate the desired heat within the process scheme. According to Papa (2000), a optimized indirect hydration process has a consumption of about 3.5 kg steam and 0.04-0.05 kWh electricity per kg of isopropanol produced.

For the direct hydration process no information is available. In order not to neglect the process energy demand for this production type, its values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the propylene oxide production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas.

For the direct hydration therefore an amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was used and for the indirect hydration a steam consumption of 3.5 kg as well as an electricity input of 0.05 kWh. For the steam production the general steam production module of this study, described in Zah & Hischier (2007), is used. A summary of all values used is given in Tab. 47.2.

Raw materials and Chemicals

For the production of isopropanol the following stoichiometric inputs are needed in the two different production methods (yield each time 100%):

- propene, $\text{CH}_3\text{CH}=\text{CH}_2$ (in both processes): 700.23 g (16.64 mol)
- sulphuric acid, H_2SO_4 (only indirect hydration): 1088.03 g (11.09 mol)

According to shown flow sheet, sulphuric acid is recycled within the process and therefore, not all of the above mentioned amount can be considered as input into the process. In Papa (2000) it is mentioned that a optimized process needs an input of about 0.35 kg H_2SO_4 per kg isopropanol produced. For this study, half of this value is used (as only the indirect hydration has this input!). For the input of propene, a yield of 95% is used for both processes in this study. To produce 1 kg isopropanol therefore 737,08 g propene are used.

The process water consumption is not quantified within the examined sources. In case of direct hydration, a stoichiometric amount of 315.3 g water (assuming a yield of 95%) is needed. As in both cases, the reaction takes place in water, an amount of ten times this stoichiometric amount is used for this

study, leading to a consumption of 0.0032 m³ per kg product. A summary of all values used is in Tab. 47.2.

Cooling water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the ethanalamines production. According to the ongoing IPPC activities of the European Commission, the cooling water demand may reach 86 kg kWh⁻¹ for an once through cooling system, which would lead to a cooling water demand of 48 kg per kg product for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m³ cooling water per kg product was used.

Transport

Standard distances and means according to Frischknecht et al. (2007b) are used for all input materials due to the fact that no information is available in Papa (2000).

47.5.3 Emissions

Waste heat

It was assumed that 100% of the electricity consumed is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of isopropanol. As approximation the air emissions occurring from the purge vent, the distillation vent and fugitive emission sources were estimated to 0.2% of the raw material input. In case of sulphuric acid, the total amount within the system is used as basis for the calculation of the lost of 0.2%.

This assumption leads to air emissions of 1.47 g of propene (for both cases) and 2.29 g of sulphuric acid (only in indirect hydration) per kg produced isopropanol. As the indirect hydration process accounts only for 50%, the latter value is divided by 2 before the integration into the dataset.

Emissions to water

The remaining amount of un-reacted propene was assumed to leave the production process with the wastewater. This assumption leads in both cases to a pollution of the wastewater with 35.38 g propene per kg product. Concerning the sulphuric acid, it is assumed that the remaining amount of added acid leaves the production with the wastewater, i.e. an amount of 347.71 g per kg produced isopropanol.

Further it was assumed that this wastewater is treated in an internal wastewater plant. Therefore, a removal efficiency of 90% for propene was assumed, leading to 3.54 g propene in the treated water. The carbon contained in the removed propene was accounted as CO₂ emissions to air (99.88 g CO₂ per kg product). For the sulphuric acid within the wastewater it is assumed that this goes 100% to the treated water, i.e. that it has 347.71 g SO₄²⁻ per kg product in the treated water. The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of propene in the treated waste

water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used.

A summary of the values used in this inventory is given in Tab. 47.2.

Solid wastes

Solid wastes occurring during the production of isopropanol were neglected in this inventory.

Tab. 47.2 Energy demand, resource demand and emissions for the production of isopropanol

[per kg isopropanol]			Remark
INPUTS			
propene	kg	7.37E-01	stoechiometric calc., 95% yield
sulphuric acid	kg	0.175	optimised proces [Papa 2000]
Water, unspecified	m3	3.20E-03	estimation as 10x stoechiometric amount
Electricity, medium voltage	kWh	1.92E-01	estimation
Natural gas, burned in industrial furnace >100kW	MJ	1	estimation
steam, at plant	kg	1.75	optimised proces [Papa 2000]
Water, cooling, unspecified	m3	2.40E-02	estimation
Transport, by train	tkm	5.47E-01	standard distances & means
Transport, by lorry	tkm	9.12E-02	standard distances & means
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	6.90E-01	calculated from electricity input
propene, to air	kg	1.47E-03	estimated as 0.2% of input
sulphate, to air	kg	1.15E-03	estimated as 0.2% of stoechiometric amount
carbon dioxide, fossil, to air	kg	9.99E-02	from waste water treatment
propene, to water	kg	3.54E-03	calculated from mass balance
sulphate (SO_4^{2-}), to water	kg	1.74E-01	calculated from mass balance
COD, BOD	kg	1.43E-01	calculated from water emissions
TOC, DOC	kg	3.03E-02	calculated from water emissions

47.5.4 Infrastructure

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg isopropanol was included.

47.6 Data quality considerations

The following table shows the data quality indicators for the inventory of the isopropanol production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the isopropanol production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoechiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the

stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data.

Tab. 47.3 Input / Output and uncertainty values for the process “isopropanol, at plant (RER)”

Explanation	Name	Location	Unit	isopropanol, at plant		uncertaintyType standardDeviation95%	GeneralComment
				RER	kg		
				Location	InfrastructureProcess Unit		
Resource Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	Water, unspecified natural origin		m3	3.20E-03	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	propylene, at plant	RER	kg	7.37E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	sulphuric acid, liquid, at plant	RER	kg	1.75E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	electricity, medium voltage, production UCTE, at grid heat, natural gas, at industrial furnace >100kW	UCTE	kWh	1.92E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	steam, for chemical processes, at plant	RER	MJ	1.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	chemical plant, organics	RER	kg	1.75E+00	1	1.46	(4,5,1,5,3,5); Estimation from Ullmann's
	transport, freight, rail	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation
	transport, freight, lorry 32t	RER	tkm	5.47E-01	1	2.09	(4,5,na,na,na,na); standard distances
		RER	tkm	9.12E-02	1	2.09	(4,5,na,na,na,na); standard distances
Output Air emission Water emission	isopropanol, at plant	RER	kg	1			
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input
	Carbon dioxide, fossil		kg	9.99E-02	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	Sulfate		kg	1.15E-03	1	2.32	(5,5,na,na,na,5); estimation
	Propene		kg	1.47E-03	1	2.32	(5,5,na,na,na,5); estimation
	BOD5, Biological Oxygen Demand		kg	1.43E-01	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	COD, Chemical Oxygen Demand		kg	1.43E-01	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	DOC, Dissolved Organic Carbon		kg	3.03E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	TOC, Total Organic Carbon		kg	3.03E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	Sulfate		kg	1.74E-01	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.
	Propene		kg	3.54E-03	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.

47.7 Cumulative results and interpretation

Results of the cumulative inventory of both datasets can be downloaded from the database.

47.8 Conclusions

The inventory for isopropanol is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if isopropanol is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

47.9 EcoSpold Meta Information

ReferenceFunction	Name	isopropanol, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Isopropanol, ab Werk
ReferenceFunction	Synonyms	2-propanol
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid isopropanol. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	67-63-0
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from propylene by indirect (50%) or direct (50%) hydration with a process yield of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	1. Mt worldwide in 1996
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

47.10 References

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48 Linear alkylbenzene

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Review: Heiko Kunst, TU Berlin

48.1 Introduction

Linear alkylbenzene, LAB – also called soft alkylate or detergent alkylate – is produced by alkylating benzene with n-paraffins or linear alpha-olefins containing between 10 and 14 C atoms (SRI International (2003)). According to UOP LLC (2001), LAB is the most common raw material for the production of detergents. Usually, LAB are liquid at room temperature – having a melting point in the area of -50 °C and a boiling point in the area of 170°C (Häussinger et al. (2000)). For this inventory the functional unit is 1 kg liquid linear alkylbenzene.

48.2 Reserves and Resources of material

The production of linear alkylbenzene (LAB) is made out of different types of hydrocarbons (for more details see the system characterization below). Therefore, all further discussion of resources equals to the discussion about these hydrocarbons as well as the discussion about raw oil in general (see according report of this study).

48.3 Use of material / product

According to all used data sources, LAB is almost entirely used for the production of LAS (linear alkylate sulfonates), the worldwide most important synthetic surfactant. According to Kocal et al. (2001), the worldwide LAB production is in the order of 2.4 kt.

48.4 Systems characterization

In the production process for linear alkylbenzene the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of linear alkylbenzene is not considered to be high. For this inventory the functional unit is 1 kg of liquid linear alkylbenzene. As process location Europe (RER) is used.

According to Kocal et al. (2001) several different production routes for the production of linear alkylbenzene can be distinguished:

- Chlorination of paraffins to monochloroparaffin and subsequent alkylation with benzene. As catalyst aluminium chloride is used within this reaction. A typical flow diagram of this process is shown in xy.
- Production of olefins (e.g. by chlorination of paraffins followed by dehydrochlorination, by wax cracking, by ethylene oligomerization etc.). These olefins are in a second step alkylated with benzene in the presence of hydrofluoric acid as catalyst.
- Dehydrogenation of linear paraffins to a mixture of linear olefins and subsequent alkylation with benzene. As catalyst again hydrofluoric acid is used within this reaction. The flow diagram of this reaction is shown in the next figure.

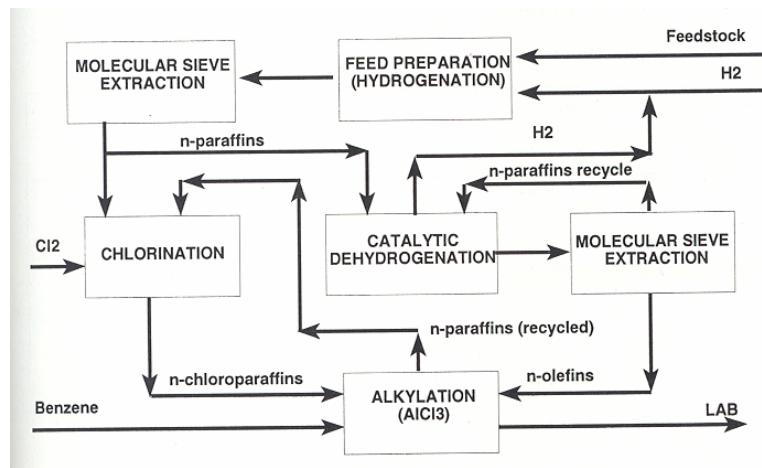


Fig. 48.1 Flow diagram for the production of LAB with aluminium chloride as catalyst (Fig.3 out of Berna et al. (1995))

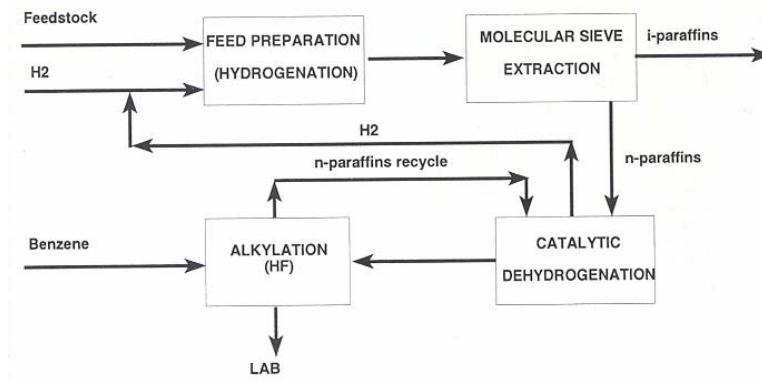


Fig. 48.2 Flow diagram for the production of LAB with hydrofluoric acid as catalyst (Fig.2 out of Berna et al. (1995))

The last of the different mentioned production ways is – again according to Kocal et al. (2001) – by far the most important one. In 2000 this production route accounted for almost 90% of the worldwide LAB production. For this study here, only the latter process route is therefore taken into account and the dataset here represents LAB produced by dehydrogenation and subsequent HF catalysed alkylation.

48.5 Linear alkylbenzene, at plant (Location: RER)

48.5.1 Process

Main source for the data is the LCI report about the production of LAS from the ECOSOL study of the European LCI Surfactant Study group (Berna et al. (1995)), representing a mix of the two above shown production ways of LAB. Its exact relation is not mentioned in Berna et al. (1995). Data from this source about the energy consumption, raw material inputs as well as the waste production have been transformed into the ecoinvent format according to the rules described in the chapter about the n-paraffins production (see Althaus et al. (2003)). Thereby it has been taken into consideration that all data described in Berna et al. (1995) represent cradle to gate inventories.

Missing information about emissions is estimated by stoichiometric calculations and mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. Due to these approximations the uncertainty within the results of this inventory are quite large. In a simplified way, the reaction can be summarized as follows:



48.5.2 Resources

Energy and Raw materials

Tab. 48.1 summarizes the resulting input and output data for the production of 1 kg LAB that can be calculated from Berna et al. (1995). The raw material input is based on the assumption that both production ways of LAB described in Berna et al. (1995) have a similar efficiency.

Tab. 48.1 Input data for the production of 1 kg of linear alkylbenzene, LAB (data from Berna et al. (1995), transformed according to the description in the chapter “n-paraffins” of Althaus et al. (2003))

[per kg linear alkylbenzene produced]		
INPUTS		
<i>raw material</i>		
n-paraffins	kg	7.16E-01
benzene	kg	3.48E-01
<i>energy</i>		
electricity	kWh	1.44E-01
heat from heavy oil	MJ	2.78E+00
heat from natural gas	MJ	1.45E+00
heat from coal	MJ	4.27E-01

Water use

There was no information available on the amount of water used for cooling esp. for the process of the LAB production. Thus, in order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the LAB production. Concerning the process water – due to a complete lack of information – an amount of 25% of the cooling water amount is used here as a first approximation.

Transport and Infrastructure

The total amount of transports of the different raw materials is calculated, based on the reported amount of transport energy. It is assumed for this study, due to a lack of more specific information, that these transports are 100% by lorry - and therefore the transport energy is only oil. According to Spielmann et al. (2007), an average European 32t lorry needs about 37 g diesel/tkm. According to Frischknecht et al. (1996), 1 t diesel needs for the production 1.07t of raw oil. Therefore, for this study, the primary amount of oil is transformed into tkm of transport using these information together with the respective heating value for oil (calculated from the relationship between the energy used in GJ and the quantity used in kg according to Berna et al. (1995)). All this results in a transport amount of 0.144 tkm per kg of produced LAB.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg linear alkylbenzene was included.

48.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 0.144 kWh, is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of linear alkylbenzene in Berna et al. (1995). As a first approximation the air emissions occurring in the different stages of the production were estimated to a total of 0.2% of the raw material input (n-paraffins and benzene).

This assumption leads to air emissions of 1.431 g n-paraffins and 0.696 g benzene.

Emissions to water

The remaining amount of unreacted raw materials was assumed to leave the production process with the wastewater. This assumption leads to a pollution of the waste water with 41.49 g n-paraffins and 20.18 g of benzene per kg LAB.

Further it was assumed that this wastewater is treated in an internal wastewater plant. Therefore, a removal efficiency of 90% for both substances was assumed, leading to 4.15 g n-paraffins and 2.02 g benzene in the treated water. The carbon contained in the removed substances was accounted as CO₂ emissions to air (leading to a total of 177.45 g CO₂ per kg product), assuming for n-paraffins an average composition of C₁₂H₂₆ (i.e. a molecular weight of 170 g/mol). The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of the remaining substances in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used.

Solid wastes

Similar to the input of energy and raw materials, the information about the produced waste is taken from the information in Berna et al. (1995). As there is no more information available about the more specific composition of this waste, it is assumed that this waste is industrial waste and - accordingly to the respective waste from APME's plastic data - is expressed by the dataset "disposal, municipal solid waste, 22.9% water, to municipal incineration" from the database ecoinvent. The amount is 2.8 g per kg of LAB produced.

48.6 Data quality considerations

The following table shows the data quality indicators for the inventory of linear alkylbenzene production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the linear alkylbenzene production has a high uncertainty, because only few data of the production processes were available. While the data for the materials and the energy demand is taken from literature, the remaining data were estimated by using stoichiometric equations and as approximation. The highest uncertainties exist thus for the emissions. Due to missing data these values are based mainly on assumptions and approximations. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 48.9.

Tab. 48.2 Input / Output and uncertainty for the process “linear alkylbenzene, at plant (RER)”

Explanation	Name	Location	Unit	alkylbenzene, linear, at plant		Uncertainty Type	Standard Deviation 95%	General Comment			
				RER 0 kg							
				Infrastructure	Process Unit						
Resources	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant				
input from Technosphere	Water, unspecified natural origin		m3	6.00E-03	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant				
	paraffin, at plant	RER	kg	7.16E-01	1	1.31	(2.5,2,1,1,5); data from ECOSOL study (Literature)				
	benzene, at plant	RER	kg	3.48E-01	1	1.31	(2.5,2,1,1,5); data from ECOSOL study (Literature)				
	heat, at hard coal industrial furnace 1-10MW	RER	MJ	4.27E-01	1	1.38	(4.5,2,1,1,5); estimation, based on ECOSOL data				
	heat, natural gas, at industrial furnace >100kW	RER	MJ	1.45E+00	1	1.38	(4.5,2,1,1,5); estimation, based on ECOSOL data				
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	2.78E+00	1	1.38	(4.5,2,1,1,5); estimation, based on ECOSOL data				
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.44E-01	1	1.38	(4.5,2,1,1,5); estimation, based on ECOSOL data				
	transport, lorry 32t	RER	tkm	1.44E-01	1	2.1	(2.5,2,1,1,5); data from ECOSOL study (Literature)				
waste	chemical plant, organics disposal, municipal solid waste, 22.9% water, to municipal incineration	RER	unit	4.00E-10	1	3.56	(5.5,1,5,4,5); estimated from a large chem. plant				
		CH	kg	2.80E-03	1	1.31	(2.5,2,1,1,5); data from ECOSOL study (Literature)				
Output	alkylbenzene, linear, at plant	RER	kg	1							
Air emission	Heat, waste		MJ	5.18E-01	1	1.31	(2.5,2,1,1,5); calculated from electricity input				
	Carbon dioxide, fossil		kg	1.77E-01	1	1.88	(5.5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Paraffins		kg	1.43E-03	1	2.32	(5.5,na,na,na,5); estimation				
Water emission	Benzene		kg	6.96E-04	1	2.32	(5.5,na,na,na,5); estimation				
	Paraffins		kg	4.15E-03	1	3.55	(5.5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Benzene		kg	2.02E-03	1	3.55	(5.5,na,na,4,5); estimated from mass balance and WWTP effic.				
	BOD5, Biological Oxygen Demand		kg	1.98E-02	1	2.11	(5.5,na,na,4,5); estimated from mass balance and WWTP effic.				
	COD, Chemical Oxygen Demand		kg	1.98E-02	1	2.11	(5.5,na,na,4,5); estimated from mass balance and WWTP effic.				
	DOC, Dissolved Organic Carbon		kg	5.38E-03	1	2.11	(5.5,na,na,4,5); estimated from mass balance and WWTP effic.				
	TOC, Total Organic Carbon		kg	5.38E-03	1	2.11	(5.5,na,na,4,5); estimated from mass balance and WWTP effic.				

48.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

48.8 Conclusions

An average European dataset for the production of linear alkylbenzene is established. This dataset is in accordance with the present quality guidelines of the ecoinvent project and is based partly on a European detergent ingredients study from the first half of the 1990s and partly on assumptions and estimations. Nevertheless, the dataset is of a reasonable quality and can be used in quite a broad context.

48.9 EcoSpold Meta Information

ReferenceFunction	Name	alkylbenzene, linear, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	This module contains material and energy input and production of waste for the production of linear alkylbenzene out of paraffin and benzene. Water consumption, emissions and infrastructure have been estimated.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Alkylbenzol, linear, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represents 1 kg of liquid linear alkylbenzene. Data are based on the ECOSOL study of the European surfactant industry.
ReferenceFunction	CASNumber	
TimePeriod	StartDate	1995
TimePeriod	EndDate	1995
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	data of published literature
Geography	Text	Data based on the European LAB production
Technology	Text	Average technology, typical for European production conditions in the mid 90s
Representativeness	Percent	
Representativeness	ProductionVolume	worldwide production: 2.4 kt
Representativeness	SamplingProcedure	Process emissions based on estimations.
Representativeness	Extrapolations	material and energy data out of ECOSOL study of European Surfactant Industry. Common translation rules used, reported in Chemical report (Althaus et al. 2003).
Representativeness	UncertaintyAdjustments	none

48.10 References

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49 Lubricants

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Review: Heiko Kunst, TU Berlin

49.1 Introduction

A common function of Lubricants is their capability of reducing friction and wear. According to Bartels et al. (2003), science has shown that around 0.4% of the gross domestic product can be saved in the Western industrialized countries only in term of energy when all tribological knowledge would be applied to lubricated processes. Therefore, lubricants are of vital interest.

49.2 Reserves and Resources of material

A huge variety of different compositions are known under the name “lubricants” – actually, 5'000 to 10'000 different formulations are used to satisfy about 90% of the different lubricants applications (Bartels et al. (2003)). In term of quantity, mineral oil components continue to be the most important ingredients. But more and more, derivatives of natural, harvestable raw materials from the oleo-chemical sector are finding their acceptance within the used substances.

49.3 Use of material / product

According to Bartels et al. (2003), in 1999 around 37 Mt of lubricants have been consumed – thereof more than half in the automotive sector (56%), and another 29% as industrial lubricants. This amount is produced by around 1700 producers worldwide. Thereof, about 200 are vertically-integrated petroleum companies where lubricants are only a minor part of their profit. Nevertheless, less than 2% of all lubricant manufacturers are producing more than 60% of the total production volume. In case of the remaining 1500 companies, lubricants are their core business.

49.4 Systems characterization

In terms of the volume, according to Bartels et al. (2003), base oils are the most important parts of lubricants as they account for more than 95%. Depending on the actual use of a lubricant, very less (1%) up to almost one third of the total lubricant constitutes out of additives. For this study, it is assumed that the production of the additives is of much lower impact and therefore their amount is not taken into account.

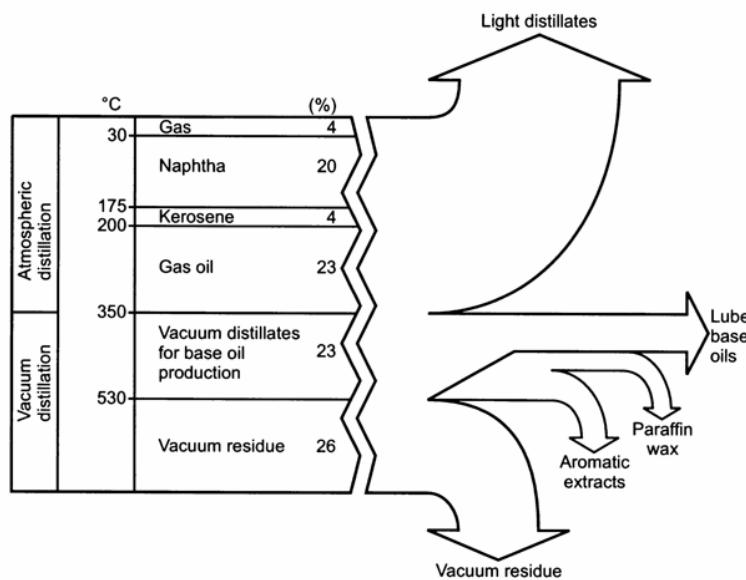


Fig. 49.1 typical yields of the different cuts from a conventional lubricating oil refining process (Figure 14 out of Bartels et al. (2003))

To achieve base oils, a variety of different steps have to be done starting with the crude oil that is extracted until the right components are isolated. Different steps therefore are e.g. refining, distillation, de-asphalting, traditional refining process, solvent dewaxing or finishing. Additional steps that are often used are as well hydrogenation and hydrocracking operations. Therefore, the above figure shows a simplified scheme of the different classes of fractions that are achieved by the first of these steps mentioned above.

Based on the fact that a multitude of different processes are possible for the production of lubricants, the following choices are done for this study here – establishing like this a typical dataset for petrochemical lubricants – therefore called “lubricants” here:

- *Hydrocracking* as basic technology for the extraction of the lubricant oils due to the fact that according to Bartels et al. (2003) more than 50% of the new manufacturing plants work with this principle.
- *Distillation and dewaxing* as subsequent process steps to achieve high-quality base lubricant oils
- *Diesel* as input due to the fact that these hydrocracker need low-sulphur oils.

For this inventory the functional unit is 1 kg of liquid lubricants. As process location Europe (RER) is used.

49.5 Lubricants, at plant (Location: RER)

This dataset includes a rough estimation of the production process for a generic kind of lubricant. Due to missing production data this inventory bases mainly on theoretical reflections. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The following assumptions and estimations are used here for the dataset of lubricants:

- **Energy:** There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data

from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the lubricants production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was used.

- **Raw material:** As raw material, diesel is used according to the assumptions described above. Due to missing quantitative information, it is in a first approximation assumed here that 1 kg of diesel is cracked into about 1 kg of hydrocarbons whereof 75% are recovered by distillation and goes to the dewaxing step. The other way round it means, that 1.333 kg diesel are used per kg of lubricant and that the remaining 0.333 kg are accounted for as by-products (light products not being within the specifications of the respective base oil produced).
- **Transport and Infrastructure:** For the transports it is assumed that these plants are in the neighbourhood of traditional refineries and therefore, no transport amounts have to be accounted for. For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and thus the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg lubricants was included.
- **Waste heat:** It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg lubricants is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.
- **Emissions to air:** There was no data available on process emissions to air for the production of lubricants. As approximation the air emissions are estimated as 1% of different hydrocarbons – expressed as unspecified hydrocarbons.
- **Emissions to water:** There was no information available about emissions to water. As the process has no process water input, it is assumed here that no emissions to water occur.
- **Solid wastes:** Solid wastes occurring during the production of lubricants were neglected in this inventory.

49.6 Data quality considerations

The following table shows the data quality indicators as well as the inventory of lubricants production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the lubricants production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 49.9.

Tab. 49.1 Input / Output and uncertainty for the process “lubricants, at plant (RER)”

Explanation	Name	Location	Unit	lubricating oil, at plant		UncertaintyType StandardDeviation95%	GeneralComment		
				RER					
				o	kg				
				Location	InfrastructureProcess				
Input from Technosphere	diesel, at regional storage	RER	kg	1.33E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 70 - 80%		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation		
Output Air emission	lubricating oil, at plant	RER	kg	1					
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input		
	NMVOC, non-methane volatile organic compounds, unspecified origin		kg	1.00E-02	1	2.32	(5,5,na,na,na,5); estimation		

49.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

49.8 Conclusions

The inventory for lubricant oil is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if lubricant oil is used in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

49.9 EcoSpold Meta Information

ReferenceFunction	Name	lubricating oil, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Schmieröl, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid lubricating oil. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production out of diesel by hydrocracking, followed by distillation and dewaxing. The overall process yield is assumed to be 75%. Inventory bases on theoretical reflexions. The emissions to air are rough estimates.
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	copper sulphate is included into the dataset as metallic copper and sulphuric acid due to the lack of an appropriate dataset for copper salt
Representativeness	UncertaintyAdjustments	none

49.10 References

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50 Maleic anhydride (2,5-Furandione)

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50.1 Introduction

This chapter describes the production of maleic anhydride. This chemical is also known as cis butene-dioic anhydride, 2,5-furandione, and toxiclic anhydride. Maleic anhydride is used primarily for the production of unsaturated polyesters.

50.2 Reserves and resources of maleic anhydride

Maleic anhydride is an organic chemical compound. It is generated from either benzene or n-butanes (or a butanes-butene mixture). Major manufacturers include Lonza, Bayer and Huntsman, among many others (Wells, 1999).

50.3 Characterisation of maleic anhydride

Maleic anhydride ($C_4H_2O_3$, CAS-No. 108-31-6) consists of white crystalline flakes that have a pungent, acrid odor. It is soluble in acetone, ether and petroleum. The most important chemical and physical properties of maleic anhydride are given in Tab. 50.1.

Maleic anhydride reacts with water to form maleic acid and will dimerize in the presence of UV light. A decomposition/polymerization reaction will occur with alkalis at elevated temperatures. It is a skin, eye and mucous membrane irritant (Wells, 1999).

Tab. 50.1 Chemical and physical properties of maleic anhydride

Property	Value	Unit
Molecular weight	98.06	g/mol
Density (at 20 °C)	1.43	kg/l
Melting point	52.85	°C
Boiling point	202	°C (sublimes)

50.4 Production and use of maleic anhydride

Maleic anhydride is produced industrially by the partial oxidation of benzene and, increasingly, by the direct oxidation of n-butanes. Both processes depend on the use of the catalysts vanadium, which may be modified with molybdenum. Some maleic anhydride is also derived as a co-product from phthalic anhydride production. As this production route is not a major contributor to world markets, it is not further described in this report.

Worldwide yearly production of maleic anhydride is around 1'500'000 tons, according to (personal communication Lonza). Major plants with capacities greater than 25'000 tons per year are located in Belgium, Germany, Italy, Russia, the US, Saudi Arabia, and Japan, according to (Wells, 1999).

According to (IPPC Chemicals, 2002), maleic anhydride is used to produce unsaturated polyesters, fumaric and maleic acid, and as an intermediate for the production of pesticides. In the US, 63% of produced maleic anhydride is used for unsaturated polyester resins, 11% as a lubricating oil additive

and 8% as copolymers. Growth through 2003 is estimated to be 2.7 percent annually (Chemical Market Reporter).

50.5 System characterization

Maleic anhydride can be produced by two routes. One route involves the partial oxidation of benzene, the other produces maleic anhydride from direct oxidation of n-butanes. The latter is the preferred route, as it is the most economical. In Europe, about 75% of maleic anhydride is produced from n-butanes 20% from benzene, and about 5% is recovered from phthalic acid production (Wells, 1999). Worldwide, about 60% of all maleic anhydride is produced from the oxidation of n-butanes (personal communication Lonza).

50.5.1 Maleic anhydride from catalytic partial oxidation of benzene

Air is preheated and compressed and mixed with benzene over a catalyst. Heat from the strongly exothermic reaction serves to produce steam (molten salts are used to remove heat). The exit gases contain maleic anhydride, carbon monoxide, carbon dioxide and traces of phenols. 50-60% of the anhydride is obtained directly from the reaction gas mixture. The remainder is recovered in the form of maleic acid. It is converted to anhydride, usually by distillation with xylene (IPPC Chemicals, 2002). Off gases leaving the scrubber are sent to a catalytic incinerator (personal communication Lonza).



The reaction occurs at slightly elevated pressure and temperatures of 350 – 450 °C. The oxidation reaction in modern plants is performed at higher concentrations of benzene in air, reducing the amount of air required by the process. This reduces the amount of electricity needed for the air compressor, which is the larger portion of the overall electricity consumption, according (personal communication Lonza).

50.5.2 Maleic anhydride from the direct oxidation of n-butanes

Air is mixed with superheated butane and feed into a reactor containing catalysts. The reaction is highly exothermic and is used to produce steam. The reaction gases are cooled and maleic anhydride is condensed and removed from the vapor stream. This is carried out quickly in order to avoid the production of maleic acid formed from the water in the reaction gases. Maleic acid is also recovered from the water scrubber. Waste gases are burned. (Wells, 1999)



The reaction occurs at slightly elevated pressure and temperatures of 400 – 430 °C. In the reaction area, n-butane and air can be fed to a fluid-bed catalytic reactor to produce maleic anhydride. Cooling coils are included in the fluid bed to generate high-pressure steam. N-butane can also be vaporized, mixed with air and catalytically oxidized in a fixed bed tubular reactor. (Lonza maleic website).

50.6 Life cycle Inventories for maleic anhydride

The information on maleic anhydride in Ecoinvent recognizes that the production processes are highly exothermic and produce steam as a co-product. There are therefore a total of seven inventories that refer to the production of maleic anhydride. Two of them refer to the multi-output production processes (partial oxidation of benzene, direct oxidation of n-butanes), four will describe the outcomes of each

process and a final inventory is a mix of both maleic anhydride products from each process, based on the European production mix of roughly 75% from n-butanes and 25% from benzene.

Tab. 50.2 Processes and outputs associated with maleic anhydride production

Inventory name	ID number	Description
maleic anhydride, at plant	2820	European mix of maleic anhydride, 25% ID No 5905, 75% ID-No 5907
catalytic oxidation of benzene	5903	Multi-output process that produces 5905 and 5906
direct oxidation of n-butane	5904	Multi-output process that produces 5907 and 5908
maleic anhydride from catalytic oxidation of benzene, at plant	5905	Output from MO-process 5903
steam from catalytic oxidation of benzene, at plant	5906	Output from MO-process 5903
maleic anhydride from the direct oxidation of n-butane, at plant	5907	Output from MO-process 5903
steam from direct oxidation of n-butane, at plant	5908	Output from MO-process 5903

50.6.1 Precursor materials and fuels consumption

Tab. 50.3 Resource consumption and energy balance for maleic anhydride production

	Catalytic oxidation of benzene	Direct oxidation of n-butanes
Yield (Wells, 1999)	88%	63%
Precursor consumption (kg / ton maleic anhydride) (Personal communication Lonza)	1136 (benzene)	1105 (n-butanes)
Net steam export (ton / ton 100% formaldehyde product) (Personal communication Lonza)	6.5	7
Electricity consumption (kWh / ton maleic anhydride) (Personal communication Lonza)	600	1200

Based on average prices for both steam production and maleic anhydride, the split for allocating environmental burdens to steam and maleic anhydride is roughly 1:9, based on (personal communication Lonza). This means that the ratio of mass x price of steam production divided by the sum of mass x price for steam and maleic anhydride production gives roughly ten percent. Thus, the steam generated by the maleic anhydride processes can be viewed as a co-product (in general, a cut-off in the range of five percent is used as a determining factor).

50.6.2 Air emissions

The off-gases are incinerated (catalytic or thermal). The figures mentioned below do not include fugitive emissions of benzene, maleic acid and maleic anhydride, which arise from storage and handling (IPPC Chemicals, 2002).

CO₂ is not removed from the off-gases.. (Personal communication Lonza). According to (Austrian UBA, 2001), 972 kg of CO₂ are produced per ton of benzene oxidation product, as well as 680 kg car-

bon monoxide (before thermal treatment). Assuming that 99% of the carbon monoxide is combusted to CO₂, this would amount to an additional 1'052 tons of CO₂ emitted.

Tab. 50.4 Air emission factors for maleic anhydride (g/kg) (Austrian UBA, 2001), Tables 34, 36

Substance	Benzene oxidation process	n-butanes process *
CO ₂	2'025	4'210 **
TOC ***	ng	0.04
NO _x	ng	0.1

* Assuming a production capacity of 19'000 tons annually as a basis for calculating emissions

** stems from combustion of unreacted butane and from CO

*** assumes benzene for the benzene oxidation process and butane for the butane oxidation process

50.6.3 Wastewater emissions (IPPC Chemicals, 2002)

IPPC Chemicals (2002), Table 3.10 indicates the following values:

Tab. 50.5 Wastewater emission factors for maleic anhydride production (g/kg)

Substance	Pre-treatment	Post-treatment
COD	1-10	0.275*

* a biological treatment efficiency of 95% is assumed

50.6.4 Liquid wastes (IPPC Chemicals, 2002)

None given.

50.6.5 Solid wastes (IPPC Chemicals, 2002)

The main solid wastes are spent catalysts. No values are given. The catalysts may consist of various types of metals.

50.6.6 Infrastructure and transports

No information was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.000000004 units per kg of produced maleic anhydride.

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

50.7 Data quality considerations

The data quality is considered to be good, and the information presented in this report reflects current BAT (best available technology) in Europe. This cannot be said for other areas, where production is shared by minor players, adopting domestic technologies with small production capacities installed.

The following table summarizes the input and output data as well as the uncertainties used for the production of maleic anhydride from both the benzene and the n-butanes oxidation processes. Addition-

ally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 50.10.

Tab. 50.6 Input / output data for maleic anhydride production by catalytic oxidation of benzene

Explanations	Name	Location	Unit	catalytic oxidation of benzene	Uncertainty Type	Standard Deviation 95%	General Comment	maleic anhydride from catalytic oxidation of benzene, at plant	steam from catalytic oxidation of benzene, at plant
								RER	RER
	Location			RER				No	No
	Infrastructure Process			0				kg	kg
	Unit			kg					
Input from Technosphere	benzene, at plant	RER	kg	1.14E+00	1	1.22	(2,2,1,1,1,5); precursor	90	10
	chemical plant, organics	RER	unit	4.00E-10	1	1.22	(2,2,1,1,1,5); infrastructure	90	10
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	6.00E-01	1	1.30	(1,5,1,1,1,5); power	90	10
	transport, freight, rail	RER	tkm	6.82E-01	1	1.30	(4,2,1,1,1,5); transport	90	10
	transport, lorry 32t	RER	tkm	1.13E-01	1	1.30	(4,2,1,1,1,5); transport	90	10
air emission	Benzene	-	kg	4.00E-05	1	1.38	(4,5,1,1,1,5); emission	90	10
	Carbon dioxide, fossil	-	kg	2.00E+00	1	1.22	(2,2,1,1,1,5); emission	90	10
	Heat, waste	-	MJ	2.17E+00	1	1.31	(2,5,1,1,1,5); waste heat	90	10
water emission	BOD5, Biological Oxygen Demand	-	kg	2.75E-02	1	1.22	(2,3,1,1,1,5); wastewater emission	90	10
COD, Chemical Oxygen Demand	-	kg	2.75E-02	1	1.22	(2,3,1,1,1,5); wastewater emission	90	10	
Outputs	maleic anhydride from catalytic oxidation of benzene, at plant	RER	kg	1				100	0
	steam from catalytic oxidation of benzene, at plant	RER	kg	6.5				0	100

Tab. 50.7 Input / output data for maleic anhydride production by direct oxidation of butanes

Explanations	Name	Location	Unit	direct oxidation of n-butane	Uncertainty Type	Standard Deviation 95%	General Comment	maleic anhydride from the direct oxidation of n-butane, at plant	steam from direct oxidation of n-butane, at plant
								RER	RER
	Location			RER				No	No
	Infrastructure Process			0				kg	kg
	Unit			kg					
Input from Technosphere	chemical plant, organics	RER	unit	4.00E-10	1	1.216459	(2,2,1,1,1,5); infrastructure	90	10
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.20E+00	1	1.300069	(1,5,1,1,1,5); power	90	10
	propane/ butane, at refinery	RER	kg	1.10E+00	1	1.22	(2,2,1,1,1,5); precursor	90	10
	transport, freight, rail	RER	tkm	6.82E-01	1	1.305929	(4,2,1,1,1,5); transport	90	10
	transport, lorry 32t	RER	tkm	1.13E-01	1	1.305929	(4,2,1,1,1,5); transport	90	10
air emission	Butane	-	kg	4.00E-05	1	1.22	(2,2,1,1,1,5); emission	90	10
	Carbon dioxide, fossil	-	kg	4.30E+00	1	1.216459	(2,2,1,1,1,5); emission	90	10
	Heat, waste	-	MJ	4.36E+00	1	1.305929	(2,5,1,1,1,5); waste heat	90	10
water emission	BOD5, Biological Oxygen Demand	-	kg	2.75E-02	1	1.22	(2,2,1,1,1,5); emission	90	10
COD, Chemical Oxygen Demand	-	kg	2.75E-02	1	1.22	(2,2,1,1,1,5); emission	90	10	
Outputs	maleic anhydride from the direct oxidation of n-butane, at plant	RER	kg	1				100	0
	steam from direct oxidation of n-butane, at plant	RER	kg	7				0	100

Tab. 50.8 Input / output data for maleic anhydride production in Europe

Explanations	Name	Location	Unit	maleic anhydride, at plant	Uncertainty Type	Standard Deviation 95%	General Comment	maleic anhydride from catalytic oxidation of benzene, at plant	steam from catalytic oxidation of benzene, at plant
								RER	RER
	Location			RER				No	No
	Infrastructure Process			0				kg	kg
	Unit			kg					
Input from Technosphere	maleic anhydride from catalytic oxidation of benzene, at plant	RER	kg	0.25	1	1.21	(1,1,1,1,1,5); maleic anhydride from catalytic oxidation of benzene		
	maleic anhydride from the direct oxidation of n-butane, at plant	RER	kg	0.75	1	1.21	(1,1,1,1,1,5); maleic anhydride from the direct oxidation of n-butane, at plant		
Output	maleic anhydride, at plant	RER	kg	1					

50.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

50.9 Conclusions

The inventories for maleic anhydride are based on industry sources, estimations and assumptions. The datasets are in accordance with the present quality guidelines of the ecoinvent project. The data are thus of a reasonable quality and can be used in quite a broad context.

50.10 EcoSpold Meta Information

ReferenceFunction	Name	catalytic oxidation of benzene	direct oxidation of n-butane	maleic anhydride, at plant
Geography	Location	RER	RER	RER
ReferenceFunction	InfrastructureProcess	0	0	0
ReferenceFunction	Unit	kg	kg	kg
ReferenceFunction	IncludedProcesses	all precursors, transports and infrastructure are included	all precursors, transports and infrastructure are included	all precursors, transports and infrastructure are included
ReferenceFunction	Amount	1	1	1
ReferenceFunction	LocalName	Katalytische Oxidation von Benzol	Direkte Oxidation von n-Butan	Maleinsäureanhydrid, ab Werk
ReferenceFunction	Synonyms			
ReferenceFunction	GeneralComment	Multi-output process, is one of two processes that produce both maleic anhydride and steam. The values presented in this report may be considered BAT (best available technology) and reflect current practices in Europe.	Multi-output process, is one of two processes that produce both maleic anhydride and steam. The values presented in this report may be considered BAT (best available technology) and reflect current practices in Europe.	Maleic anhydride and steam are coproducts produced by the direct oxidation of butanes.
ReferenceFunction	CASNumber			108-31-6
TimePeriod	StartDate	1997	1997	1997
TimePeriod	EndDate	2000	2000	2000
TimePeriod	DataValidForEntirePeriod	1	1	1
TimePeriod	OtherPeriodText			
Geography	Text	RER	RER	RER
Technology	Text	represents a current cross-section of actual plants in Europe	represents a current cross-section of actual plants in Europe	represents a current cross-section of actual plants in Europe
Representativeness	Percent			
Representativeness	ProductionVolume	unknown	unknown	unknown
Representativeness	SamplingProcedure	see technology	see technology	see technology
Representativeness	Extrapolations	none	none	none
Representativeness	UncertaintyAdjustments	none	none	none

50.11 References

- Chemical Market Reporter a publication of the Schnell Publishing Company, a member of the Reed Elsevier group
- Frischknecht et al. (2007) Frischknecht R., Althaus H.-J., Doka G., Dones R., Hischier R., Hellweg S., Jungbluth N., Kellenberger D., Nemecek T., Rebitzer G. and Spielmann M. (2007) Overview and Methodology. Final report ecoinvent Data v2.0 No. 1. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.
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51 Melamine

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 Review: Heiko Kunst, TU Berlin
 Last Changes: 2006

51.1 Introduction

Melamine ($C_3H_6N_6$, CAS-No. 108-78-1) is at room temperature a fine white powdered crystal (Crews & Ripperger (2001)). Its solubility in water is depending from temperature. For this inventory the functional unit is 1 kg solid melamine. The most important chemical and physical properties of melamine used in this inventory are given in Tab. 51.1.

Synonyms for melamine: 2,4,6-triamino-1,3,5-triazine

Tab. 51.1 Chemical and physical properties of melamine (according to Crews & Ripperger (2001))

Property	Unit	Value	Remarks
Molecular weight	$g\ mol^{-1}$	126.13	
Density	$g\ cm^{-3}$	1.573	at room conditions
Melting point	°C	350	at normal pressure

51.2 Reserves and Resources of material

Until the beginning of the 60s, melamine was according to Crews & Ripperger (2001) only out of di-cyandiamide. Since then, these production sites have almost all either been closed down or then they changed to the urea process, discovered in the 40s by Mackay. Therefore, all further discussion of resources equals to the discussion about urea and therefore you can refer to the agricultural-report.

51.3 Use of material / product

According to Crews & Ripperger (2001) is most melamine used for the reaction with formaldehyde for the production of resins for laminating and adhesive applications. There, one of the most important applications is the use of melamine for the upper sheet e.g. of tabletops. A second important use of melamine is its function as amino cross-linker in heat-cured systems – e.g. in the automotive industry. Furthermore, this substance has also its applications in other fields like wet-strength resins for paper industry, ion-exchange resins, plastic moulding compounds or fire retardants in PUR foam. Tab. 51.2 gives an overview of the estimated main applications in different regions.

Tab. 51.2 Melamine applications, in percent, by region (according to Crews & Ripperger (2001))

Application	Europe	United States	Japan
Laminates	47	35	6
Glue, adhesives	25	4	62
Molding compounds	9	9	16
Coatings	8	39	12
Paper, textiles	11	5	3
Others	-	8	1

In the beginning of the 90s, the worldwide production capacity of melamine was in the order of 550 kt. Thereof, 230 kt are in Europe, 175 kt in Middle and Far East and only 97 kt in the United States (Crews & Ripperger (2001)).

51.4 Systems characterization

In the production process for melamine the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of melamine is not considered to be high. For this inventory the functional unit is 1 kg of solid melamine. As process location Europe (RER) is used.

As already mentioned in chapter 51.2, nowadays almost 100% of melamine is produced out of urea. But also then, different production techniques can be distinguished. All of them are either high-pressure reactions without any catalysts or then catalytic reaction at low pressure. Within each of the reactions, the three steps of synthesis, melamine recovery and purification as well as off-gas treatment can be distinguished. Due to lack of data about the different methods – for this study here, a 50:50 mix of the BASF process (as representative for the low pressure reactions) and of the Montedison process (example of high pressure process) is used. Process flow schemes for these two production routes of melamine are explained in the following paragraphs and shown in Fig. 51.1 rsp. Fig. 51.2.

According to Crews & Ripperger (2001), in the first case (BASF process), alumina is used as a catalyst. The reaction temperature is about 400°C and for the fluidization, an ammonia-carbon dioxide mixture is added. The off-gas treatment has several steps that remove melamine and unreacted urea. The remaining off-gas is partly used as the above mentioned fluidization gas, partly as quenching gas in the crystallizer unit.

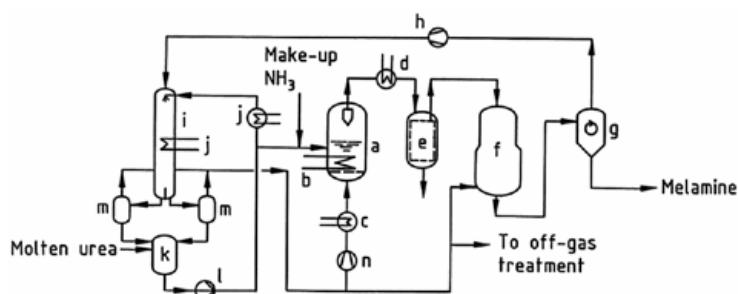


Fig. 51.1 Process chain for the production of melamine by BASF process (Fig.1 out of Crews & Ripperger (2001) – showing reactor [a], heating coils [b], fluidizing gas preheater [c], gas cooler [d], gas filter [e], crystallizer [f], cyclone [g], blower [h], urea washing tower [i], heat exchanger [j], urea tank [k], pump [l], droplet separator [m], compressor [n])

In case of the Montedison process, the operation temperature is about 370°C and the pressure is around 7 MPa. Besides urea, ammonia is also feed into the reactor. In the following quencher, this mixture is treated with an aqueous solution of ammonia and carbon dioxide resulting in a precipitation of melamine. The remaining mixture of ammonia and carbon dioxide is recycled either in a urea or in other fertilizer production sites.

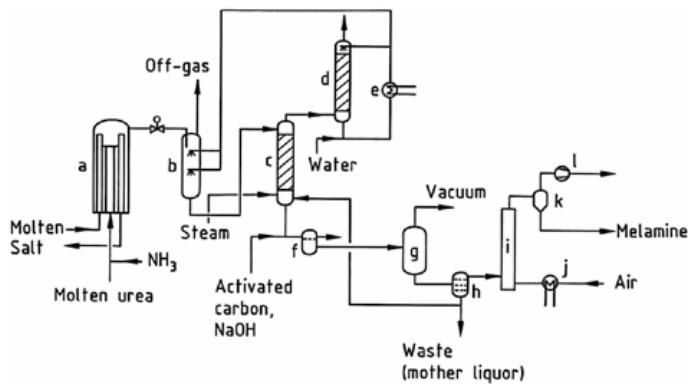


Fig. 51.2 Process chain for the production of melamine by Montedison process (Fig.4 out of Crews & Ripperger (2001) – showing reactor [a], quencher [b], stripper [c], adsorption column [d] , heat exchanger [e] & [j], filter [f] & [h], vacuum crystallizer [g], pneumatic dryer [i], cyclone [k] and blower [l])

51.5 Melamine, at plant (Location: RER)

51.5.1 Process

This dataset includes a rough estimation of the production process for melamine. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The examined production way for melamine can be summarized within the following reaction:



51.5.2 Resources

Energy

The above shown reaction is endothermic and requires about 650 kJ per mole of melamine produced. There was no further information available on the total amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the melamine production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 68.2.

Raw materials and Chemicals

According to the above shown reaction equations - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of melamine:

- urea, $\text{CH}_4\text{N}_2\text{O}$: 2856.577 g (47,57 mol)

For the production a yield of 95% for the overall reaction out of urea is used (see chapter 51.4). Therefore 3006.923 g urea are considered as raw materials in this inventory. A summary of the values used is given in Tab. 68.2.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the melamine production.

For the process water amount, due to a lack of data, an amount of 25% of the cooling water amount is assumed here – leading to an input of 6 kg water per kg melamine.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the urea input.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg melamine was included.

51.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg melamine is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of melamine. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input – urea in form of its decomposition products isocyanic acid and ammonia (Crews & Ripperger (2001)). This assumption leads to air emissions of 4.311 g isocyanic acid as well as 1.703 g ammonia.

Besides, the reaction scheme in eq. 1.1 shows that beside melamine also ammonia and carbon dioxide are produced within this process. While in the case of the Montedison process, all these substances are in a liquid solution that is recycled 100% by an urea plant, the BASF process uses only part of these gases within the process. However, it can be assumed that these remaining substances are either used in further processes on site, or that the remaining substances are recycled (see e.g. SRI Consulting (2006)). All in all, we assume for this dataset here that all further products according to eq. are either used as by-products or then are recycled and thus none of them are further taken into account within this dataset here.

Emissions to water

Again, in the Montedison process the process water leaves the plant as an input for the urea production due to the dissolved amounts of ammonia and carbon dioxide. In the BASF process, there is only one

washing tower for removal of the remaining urea used – other processes with water are not used there. Therefore for this study it is assumed that no emissions to water occur.

Solid wastes

Solid wastes occurring during the production of melamine were neglected in this inventory.

Tab. 51.3 Energy demand, Resource demand and emissions for the production of melamine.

[per kg melamine]			Remark
INPUTS			
urea	kg	3.007	stoichiometric calc., 95% yield
-> represented by "urea, as N, at regional storehouse"	kg	1.386	N is used as reference unit
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m ³	2.40E-02	estimation
Water, unspecified	m ³	6.00E-03	estimation
transport by train	tkm	1.80E+00	standard distances
transport by lorry, 32t	tkm	3.01E-01	standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
ammonia, to air	kg	1.70E-03	estimated as 0.2% of input of urea
isocyanic acid, to air	kg	4.31E-03	estimated as 0.2% of input of urea

51.6 Data quality considerations

Tab. 51.4 shows the data quality indicators for the inventory of melamine production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the melamine production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 51.9.

Tab. 51.4 Input / Output and uncertainty for the process “melamine, at plant (RER)”

Explanation	Name	Location	Unit	melamine, at plant RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment	
							Location	InfrastructureProcess
							Unit	
Resource	Water, cooling, unspecified natural origin	RER	m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	Water, unspecified natural origin		m3	6.00E-03	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
Input from Technosphere	urea, as N, at regional storehouse	RER	kg	1.39E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	electricity, medium voltage, production UCTE, at grid		kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation	
	transport, freight, rail	RER	tkm	1.80E+00	1	2.09	(4,5,na,na,na,na); standard distances	
Output	transport, lorry <16t, fleet average	RER	tkm	3.01E-01	1	2.09	(4,5,na,na,na,na); standard distances	
	melamine, at plant	RER	kg	1				
Air emission	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input	
	Ammonia		kg	1.70E-03	1	2.32	(5,5,na,na,na,5); estimation	
	Isocyanic acid		kg	4.31E-03	1	2.32	(5,5,na,na,na,5); estimation	

51.7 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

51.8 Conclusions

The inventory for melamine is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if melamine is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

51.9 EcoSpold Meta Information

ReferenceFunction	Name	melamine, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Melamin, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of solid melamine. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	108-78-1
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	50:50 split between BASF technique and Montedison technique for the production from melamine out of urea. The overall process yield is of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) were estimated using mass balance.
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

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52 Mercury

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Last changes:

2007

52.1 Introduction

Mercury (Hg, CAS-No. 7439-97-6), also called quicksilver, is a silvery-white, shiny metal that is liquid at room temperature (its melting point is at -38.9°C – the boiling point at 357.3°C). It has a relatively high vapour pressure and its vapour is heavier than air (Simon (2001)).

52.2 Resources and use of material

The consumption of mercury declined in the last decades steadily, mainly due to the toxicological concerns for humans but also the nature. Nevertheless, due to its special properties, a number of uses will continue to be there for this special metal. Among them are the use in thermometers, mercury vapour diffusion pumps and especially the mercury cells in the chlor-alkali electrolysis.

Mercury containing ores are usually low-grade ores – having in average only about 1% of Hg. Usually, they are close to the earth's surface and the mining depth is therefore limited. In 2000, the worldwide mined amount of Hg was in the order of 1'350 t with Spain (500 t), Kyrgyzstan (former Soviet Union, 260 t) and Algeria (240 t) being the most important mining countries (Reese (2001)). The total Hg production – including secondary production – in 1996 was in the order of 3'400 t (Sznopek & Goonan (2000)), with Western Europe being responsible for almost a third of this total.

52.3 Systems characterization

In the production process for mercury in this study the main raw materials, an approximation of the production efforts (land-use, infrastructure, energy) and estimations for emissions based on several different data sources are included. This module represents therefore only a rough estimation of the process requirements and should be used only when the impact of mercury is not considered to be high.

The whole production of primary mercury – the only mercury included into this study here – can be divided into the following steps:

- Mining of Hg-containing ores by traditional mining techniques;
- Dressing (preliminary concentration of Hg out of the extracted ores) by separating the extracted Hg mineral from other minerals by different techniques (e.g. hand-sorting, flotation) and then further crushing to a small grain size;
- Processing to metallic mercury in furnaces, retorts or muffles.

For this study, a production of mercury by open-pit mining is assumed (due to the fact that these ores are not very deep). Concerning the ore, it is assumed here that all is of the most common type, containing Hg – cinnabar (HgS). According to Jasinski (1995) it is the most often mined Hg containing ore. For the dressing a hand-sorting step is assumed, followed by a crushing step. In the last step, the ore grains are put into a furnace to recover metallic Hg. The functional unit for the inventory is 1 kg of pure liquid mercury. As process location GLO (for global) is used in this process.

52.4 Mercury, liquid, at plant (Location: GLO)

Main data source for the mercury production is Simon (2001). As this source contains quantitative information only about the third step (furnace), process data from similar processes within this study are used as a first approximation for the first two steps in mercury production:

- *Mining*: the data for the mining operation are taken from limestone mining (Kellenberger et al. (2007)). As resource “cinnabar, in ground” is used. As it is a very low-grade mineral, it is assumed here that the energy consumption is 200% compared to limestone, while all other information is taken 1:1 from limestone mining.
- *Hand sorting*: this step is assumed to contribute very little to the environmental problems of the Hg production and therefore it is not further taken into account within this study.
- *Crushing and milling*: again, data from limestone are used as a first approximation. Therefore, the data are taken from the dataset “primary crushing of limestone” as well as from the respective milling dataset in Kellenberger et al. (2007).
- *Furnace operation*: For the last step described above, several different techniques can be used, whereof here a mixture of rotary kiln and multiple-hearth furnaces is assumed due to the fact that it is quantitative information available in Simon (2001) for these two techniques. In details, this last step is included in the following way:
 - *Material input*: Besides the crushed Hg mineral, quicklime is added to bind the sulphur in solid form. As there is no quantitative information given, a stoichiometric amount (yield 95%) is assumed here. For the input amount of cinnabar – the sorted and crushed Hg-containing mineral – a overall yield of 90% is assumed in the ecoinvent project. In accordance with other metals, the input of raw material takes only cinnabar and its respective yield into account but not the other metals or the death material that is extracted as well.
 - *Energy input*: According to Simon (2001), a multiple-hearth furnace uses around 34 L oil per tonne of treated input material while a rotary kiln has an input of around 26 L oil per tonne of ore. Due to a lack of information about the throughput of the different technologies, an average value of 30 L oil (assuming heavy fuel oil) per tonne of treated ore is assumed here.
 - *Water*: For the condensation step of the furnace gas, containing the mercury, water is used here as cooling medium. Due to a lack of quantitative information, this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt (intermediates included) of different chemicals per year (Gendorf (2000)). In that plant in total 24 kg water per kg of product were used for. This value is used here as well. Furthermore it is assumed that no process water is used here.
 - *Transports and infrastructure*: It is assumed here that the whole operations are close to the mining pit – therefore only quicklime has to be transported, using standard distances (600 km train, 100 km lorry). For the infrastructure, the process “glass production site” is used as a first approximation due to the fact that this dataset contains a furnace.
 - *Emissions to air*: There was no data available on process emissions to air in Simon (2001). In Sznopek & Goonan (2000) it is reported that in 1990, a mercury mine production of 448 t was responsible for a loss to the environment of 72 t during milling and roasting operations. Assuming that these emissions were mainly to air, this leads to air emissions of 0.161 kg per kg of Hg produced.
 - *Emissions to water / Waste*: There was no information available. But it can be assumed that there is no relevant release to water.

- *Waste / by-products:* Also here, no quantitative information is available. It is assumed that the produced calcium sulphate can be used for further processes. As it is considered as a by-product, it is not further taken into account within this dataset.

Tab. 52.1 Input and output data for the production of 1 kg of liquid mercury

Materials / Energy / Emissions		per kg mercury	Remarks
Input			
cinnabar, in ground	kg	1.29E+00	assuming a overall yield of 90%
quicklime	kg	2.94E-01	stoichiometric calculation, yield 95%
occupation, mineral extraction site	m2a	9.83E-05	estimation, based on limestone production
transformation, to mineral extraction site	m2	7.56E-06	dito
transformation, from forest	m2	7.56E-06	dito
recultivation, limestone mine	m2	7.56E-06	dito
water, well, in ground	m3	3.40E-05	dito
blasting	kg	8.97E-05	dito
diesel, burned in building machine	MJ	2.09E-02	dito
light fuel oil, low sulphur, burned in boiler 100 kw	MJ	4.62E-03	dito
heat, light fuel oil, at industrial furnace	MJ	8.98E-02	dito
heat, heavy fuel oil, at industrial furnace	MJ	1.24E+03	average for furnace from Simon (2001)
mine, limestone	unit	6.09E-11	estimation, based on limestone production
glass production site	unit	1.25E-10	approximation for Hg-furnace
industrial machine, heavy, unspecified, at plant	kg	2.32E-04	estimation, based on crushing and milling
conveyor belt, at plant	m	3.22E-08	estimation, based on limestone crushing
electricity, medium voltage, UCTE mix	kWh	3.26E-02	estimation, based on crushing and milling
transport, by train	tkm	1.77E-01	quicklime transport over standard distance
transport, by lorry	tkm	2.94E-02	quicklime transport over standard distance
cooling water, unspecified origin	m3	2.40E-02	estimation, based on Gendorf 2000
Output			
waste, heat		0.00E+00	calculated from electricity input
particulates, > 10 um	kg	1.40E-04	estimation, based on limestone production
particulates, > 2.5 um and < 10 um	kg	5.55E-05	dito
particulates, < 2.5 um	kg	1.03E-05	dito
mercury, to air	kg	1.61E-01	estimation, based on Sznopek (2000)

52.5 Data quality considerations

The uncertainty scores established according to the method used in this study (see Frischknecht et al. (2007)) include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Here data from limestone production are used as an approximation for the first two steps of the mercury production and therefore especially reliability, completeness and further technological correlation have higher values, resulting in a relative high uncertainty for the whole process. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 52.8.

Tab. 52.2 Input / Output and uncertainty for the process “mercury, liquid, at plant (GLO)”

Explanations	Name	Unit	mercury, liquid, at plant	uncertaintyType StandardDeviation 95%	GeneralComment		
					GLO	0	
					Location	InfrastructureProcess	Unit
Technosphere	blasting	kg	8.97E-5	1	1.40	(4,3,1,3,3,5); approximation with data from lime production	
	electricity, medium voltage, production UCTE, at grid	kWh	3.26E-2	1	1.40	(4,3,1,3,3,5); approximation with data from lime production	
	diesel, burned in building machine	MJ	2.09E-2	1	1.40	(4,3,1,3,3,5); approximation with data from lime production	
	light fuel oil, burned in boiler 100kW, non-modulating	MJ	4.62E-3	1	1.40	(4,3,1,3,3,5); approximation with data from lime production	
	heat, light fuel oil, at industrial furnace 1MW	MJ	8.98E-2	1	1.40	(4,3,1,3,3,5); approximation with data from lime production	
	industrial machine, heavy, unspecified, at plant	kg	2.32E-4	1	3.10	(4,3,1,3,3,5); approximation with data from lime production	
	conveyor belt, at plant	m	3.22E-8	1	3.10	(4,3,1,3,3,5); approximation with data from lime production	
	heat, heavy fuel oil, at industrial furnace 1MW	MJ	1.24E+3	1	1.50	(4,5,1,5,3,5); according to quantitative information in Ullmann's	
	recultivation, limestone mine	m2	7.56E-6	1	3.10	(4,3,1,3,3,5); approximation with data from lime production	
	mine, limestone	unit	6.09E-11	1	3.10	(4,3,1,3,3,5); approximation with data from lime production	
	quicklime, milled, loose, at plant	kg	2.94E-1	1	1.40	(4,3,1,3,3,5); estimation based on an assumed yield of 100% for furnace	
	glass production site	unit	1.25E-10	1	3.80	(4,5,1,3,5,4); estimation	
	transport, freight, rail	tkm	1.77E-1	1	2.10	(4,5,na,na,na,na); standard distances	
	transport, lorry>16t, fleet average	tkm	2.94E-1	1	2.10	(4,5,na,na,na,na); standard distances	
resources	Water, well, in ground	m3	3.40E-5	1	1.40	(4,3,1,3,3,5); approximation with data from lime production	
	Water, cooling, unspecified natural origin	m3	2.40E-2	1	1.90	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	Occupation, mineral extraction site	m2a	9.83E-5	1	1.70	(4,3,1,3,3,5); approximation with data from lime production	
	Transformation, to mineral extraction site	m2	7.56E-6	1	2.20	(4,3,1,3,3,5); approximation with data from lime production	
	Transformation, from forest	m2	7.56E-6	1	2.20	(4,3,1,3,3,5); approximation with data from lime production	
	Cinnabar, in ground	kg	1.29E+0	1	1.40	(4,3,1,3,3,5); based on assumed overall yield of 90%	
emission to air	Heat, waste	MJ	1.17E-1	1	1.40	(4,3,1,3,3,5); calculated from electricity input	
	Particulates, > 10 um	kg	1.40E-4	1	1.70	(4,3,1,3,3,5); approximation with data from lime production	
	Particulates, > 2.5 um, and < 10 um	kg	5.55E-5	1	2.20	(4,3,1,3,3,5); approximation with data from lime production	
	Particulates, < 2.5 um	kg	1.03E-5	1	3.10	(4,3,1,3,3,5); approximation with data from lime production	
Output	Mercury	kg	1.61E-1	1	5.20	(4,5,1,5,3,5); according to quantitative information in literature	
	mercury, liquid, at plant	kg	1.00E+0				

52.6 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

52.7 Conclusions

The inventory for mercury is based on estimations and assumptions, starting with the dataset for limestone. The unit process raw data are meant to be used as background information if mercury is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

52.8 EcoSpold Meta Information

ReferenceFunction	401	Name	mercury, liquid, at plant
Geography	662	Location	GLO
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	402	IncludedProcesses	Raw materials, machineries and energy consumption for production, estimated emissions to air from production and infrastructure of the site (approximation). No water emissions.
ReferenceFunction	404	Amount	1
ReferenceFunction	490	LocalName	Quecksilber, flüssig, ab
ReferenceFunction	491	Synonyms	
ReferenceFunction	492	GeneralComment	The functional unit represent 1 kg of liquid mercury. Large uncertainty of the process data due to weak data on the production process.
ReferenceFunction	502	CASNumber	7439-97-6
TimePeriod	601	StartDate	2000
TimePeriod	602	EndDate	2000
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	date of published literature
Geography	663	Text	Data used has no specific geographical origin (stoichiometry). Average European processes for raw materials, transport requirements and electricity mix used.
Technology	692	Text	Data approximated with data from lime mining, crushing and milling plus estimation of the additional furnace operation step, based on information in literature and own assumptions.
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	
Representativeness	725	SamplingProcedure	
Representativeness	726	Extrapolations	see technology
Representativeness	727	UncertaintyAdjustments	none

52.9 References

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53 Methanol from natural gas

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53.1 Introduction

Methanol (CH_3OH , CAS-No. 67-56-1, synonyms: methyl alcohol, methyl hydroxide, monohydroxymethane) is a clear, colourless, volatile liquid with a faint alcohol-like odour. Methanol is the simplest of the alcohols, having only one carbon atom, and is completely miscible in water. Methanol easily dissolves in other alcohols and chlorinated hydrocarbons, but has limited solubility in diesel fuel, vegetable oils, and aliphatic hydrocarbons (USDoE 1991). For this inventory the functional unit is 1 kg of pure methanol. The most important chemical and physical properties of methanol used in this inventory are given here.

Tab. 53.1 Chemical and physical properties of methanol

Property	Unit	Value	Remarks
Molecular weight	g mol^{-1}	32.04	
Specific gravity	kg m^{-3}	792	at 20 °C
Heat of combustion, net calorific value (LHV)	MJ kg^{-1}	20.0	
Heat of combustion, gross calorific value (HHV)	MJ kg^{-1}	22.7	

53.2 Reserves and resources of material

Commercial production of methanol is based on synthesis gas mixtures (carbon monoxide and hydrogen) derived primarily from natural gas. In recent years, a major shift in regional methanol production has occurred. Countries that have large natural gas reserves and limited domestic consumption (for example, Chile, Malaysia or Trinidad) have built world-scale methanol plants and export most of their output, leading to a restructuring of the methanol market (ChemExpo 2000). As a consequence of this development, older methanol plants in industrialized countries such as the United States, Japan, and the Federal Republic of Germany have been shut down (Ullmann 2001, Chapter 10).

All large plants currently being planned are designed for use with natural gas and some plants built for operation with naphtha have been converted. Less than 10% of the currently installed worldwide methanol production capacity is based on raw materials other than natural gas (Ullmann 2001, Chapter 10). During the Year 1997 one of the world's largest methanol plant was inaugurated in Norway (Tjeldbergodden industrial complex). It is using gas from Statoil's Heidrun field in the Norwegian Sea as feedstock, methanol production capacity of the plant is 840'000 t per year. That corresponds to 25% of the European capacity and 13% of Europe's consumption (Nitrogen & Methanol 2000).

For this assessment only the production of methanol from natural gas was investigated.

53.3 Use of material / product

In the Year 2000 the worldwide demand of methanol was estimated to be $28.2 * 10^6 \text{ t}$ which is 76% of the available production capacity (Methanol 2000). More than 70% of the methanol produced worldwide is used in chemical syntheses. In order of importance the produced methanol was used as follows:

- Formaldehyde: 9.6×10^6 t or 34% of production.
- Methyl tert-butyl ether (MTBE): 7.8×10^6 t or 28% of production.
- Acetic acid: 2.7×10^6 t or 10% of production.
- Methyl methacrylate (MMA): 0.8×10^6 t or 3% of production.
- Dimethyl terephthalate (DMT). 0.6×10^6 t or 2% of production.

Only a small proportion is used for energy production (0.6×10^6 t or 2% of production), although this use has great potential (Methanol 2000).

53.4 Systems characterization

The process methanol at plant represents an average worldwide methanol production from natural gas. The process chain was assessed as shown in the following figures. There were three processes modelled:

- Methanol, at plant (location: GLO), see Fig. 53.1
- Methanol, at regional storage (location: CH); see Fig. 53.2
- Methanol plant (location: GLO); see Fig. 53.3

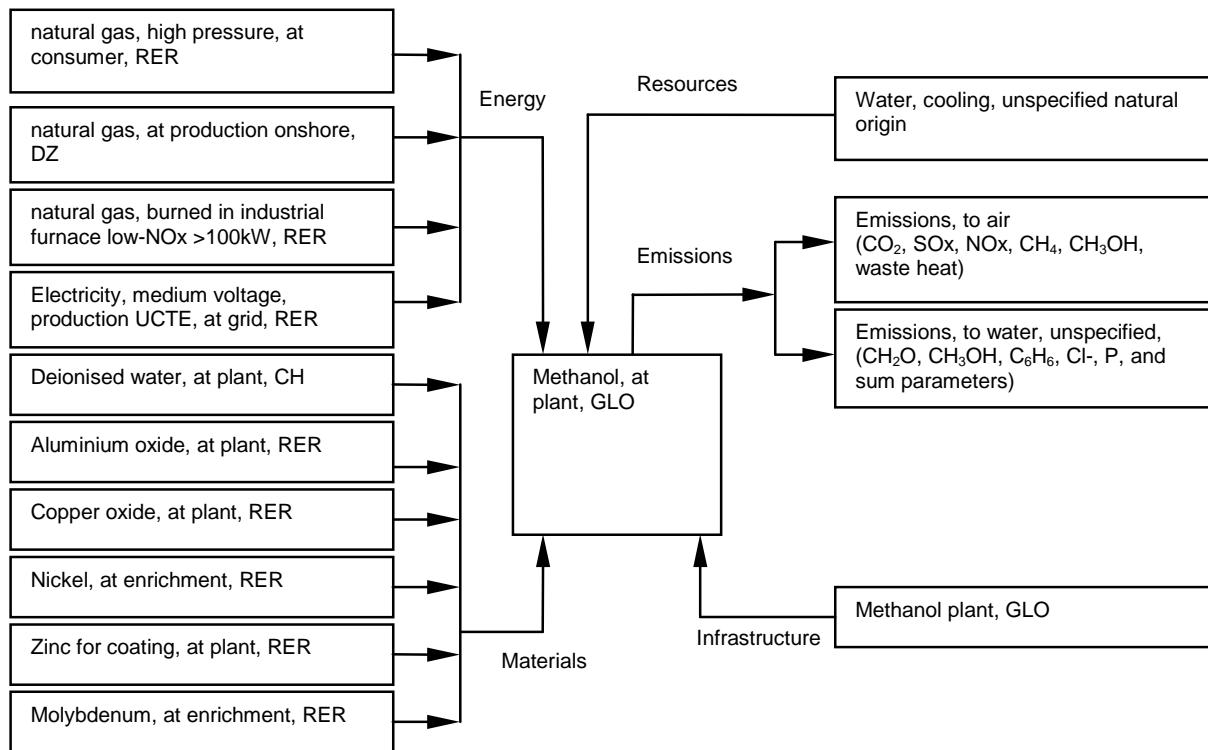


Fig. 53.1 Process chain for the production of methanol

Methanol at plant

For this process, natural gas is used as feedstock (processes used: natural gas, high pressure, at consumer, RER and natural gas, at production onshore, DZ) and in the furnace (process: natural gas,

burned in industrial furnace low-NOx >100kW, RER). In these preceding processes the whole process chain of natural gas is included.

Resources of minor importance are electricity, cooling water and boiler feed water (deionised). Also accounted as resource is the catalysts used in the process. As output there is only methanol to account. The spent catalysts were assumed to be recycled and therefore not considered as wastes. Further it was assumed that the surplus hydrogen leaving the process is burned in the furnace. Most emissions to the air are already included in the preceding process of the furnace. The only additional emissions to the air considered are sulphur dioxide from desulphurisation of the feed, and nitric oxide emissions caused by the combustion of hydrogen. Also most of the waste heat is already included in the preceding process of the furnace. The only additional waste heat considered is the waste heat of the burned hydrogen and of the used electricity. There are two types of wastewaters: first, cooling water, which is only slightly polluted and, second, wastewater of the distilling column, which is polluted with hydrocarbons.

Methanol at regional storage

Transport from the plant to a regional storehouse, which is representative for the use of methanol in Switzerland, was considered. The amounts of transport processes needed were calculated with the distances from the relevant plant sites or production areas and the used carrier (tanker, train, lorry). The losses of methanol occurring within the transportation and storage were considered roughly.

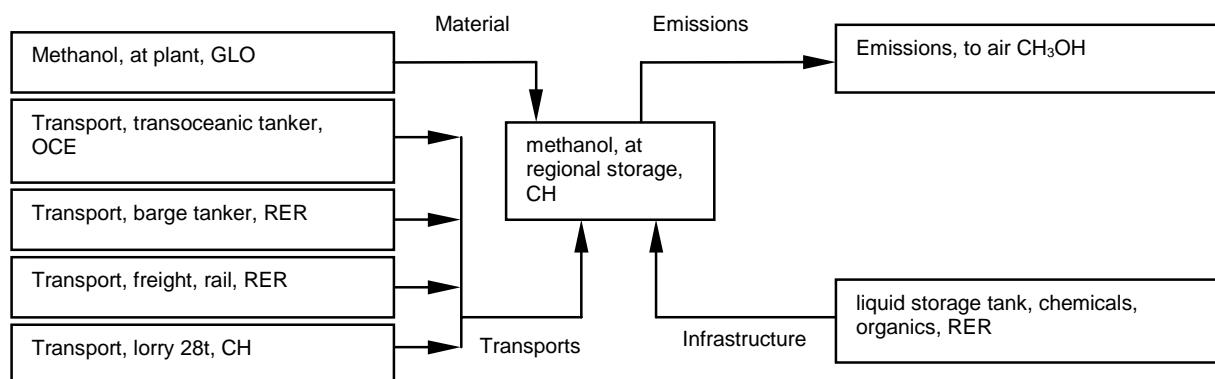


Fig. 53.2 Process chain for the process “regional methanol, at storage”

Methanol plant

For the infrastructure of the methanol plant, modules for the construction and dismantling of the buildings and the chemical equipment were used. Further the land use of the plant is also included. In this module no emissions or wastes from contamination with chemicals is included. The process chain was assessed as shown in the following figure.

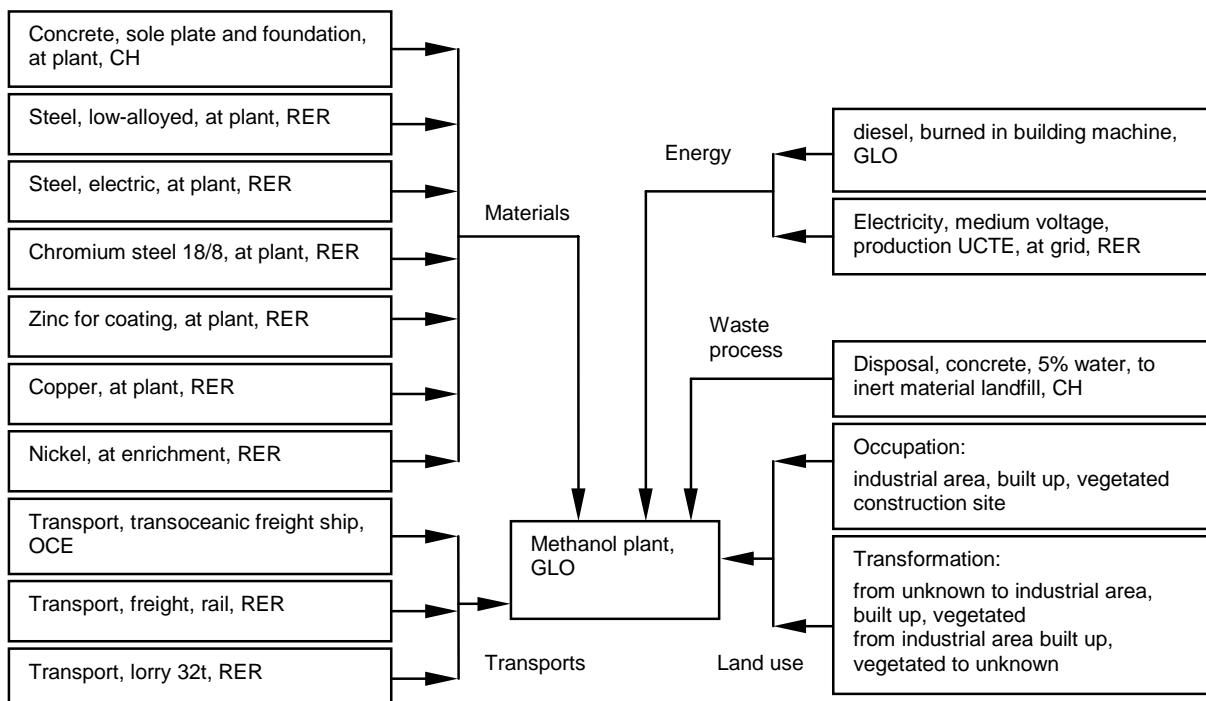


Fig. 53.3 Process chain for the methanol plant infrastructure

53.5 Methanol, at plant (location: GLO)

53.5.1 Process

For normal methanol synthesis, reforming is performed in one step in a tubular reactor at 850 – 900 °C in order to leave as little methane as possible in the synthesis gas. For large methanol synthesis plants, Lurgi has introduced a two-step combination (combined reforming process) that gives better results. In the primary tubular reformer, lower temperature (ca. 800 °C) but higher pressure (2.5-4.0 MPa instead of 1.5-2.5 MPa) are applied.

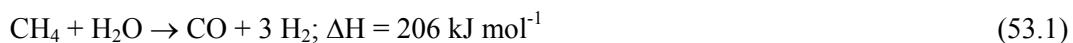
More recently, Lurgi developed another two-step gas production scheme. It is based on catalytic auto-thermal reforming with an adiabatic performer and has economical advantages for very large methanol plants. At locations where no carbon dioxide is available most of the methanol plants are based on the following gas production technologies, depending on their capacities: steam reforming for capacities up to 2000 t d⁻¹ or combined reforming from 1800 to 2500 t d⁻¹ (Ullmann 2001).

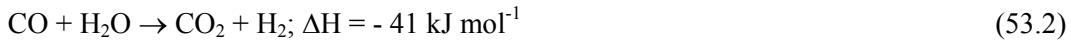
For the energy and resource flows in this inventory a modern steam reforming process was taken as average technology. To estimate best and worst case values, also values from combined reforming and autothermal reforming were investigated.

Methanol produced using a low pressure steam reforming process (ICI LPM) accounts for approximately 60% of the world capacity (Syntex 2000a). A simplified process scheme of methanol production with steam reforming is shown in Fig. 53.4. Besides steam reforming, especially combined reforming has gained importance due to the production of methanol in large plants at remote locations.

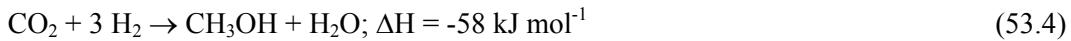
The reaction of the steam-reforming route can be formulated for methane, the major constituent of natural gas, as follows:

Synthesis gas preparation:





Methanol synthesis:



For an average plant the total carbon efficiency is around 75%, 81% for the synthesis gas preparation and 93% for the methanol synthesis (Le Blanc et al. 1994, p. 114). For steam reformers usually a steam to carbon ratio of 3:1 to 3.5:1 is used.

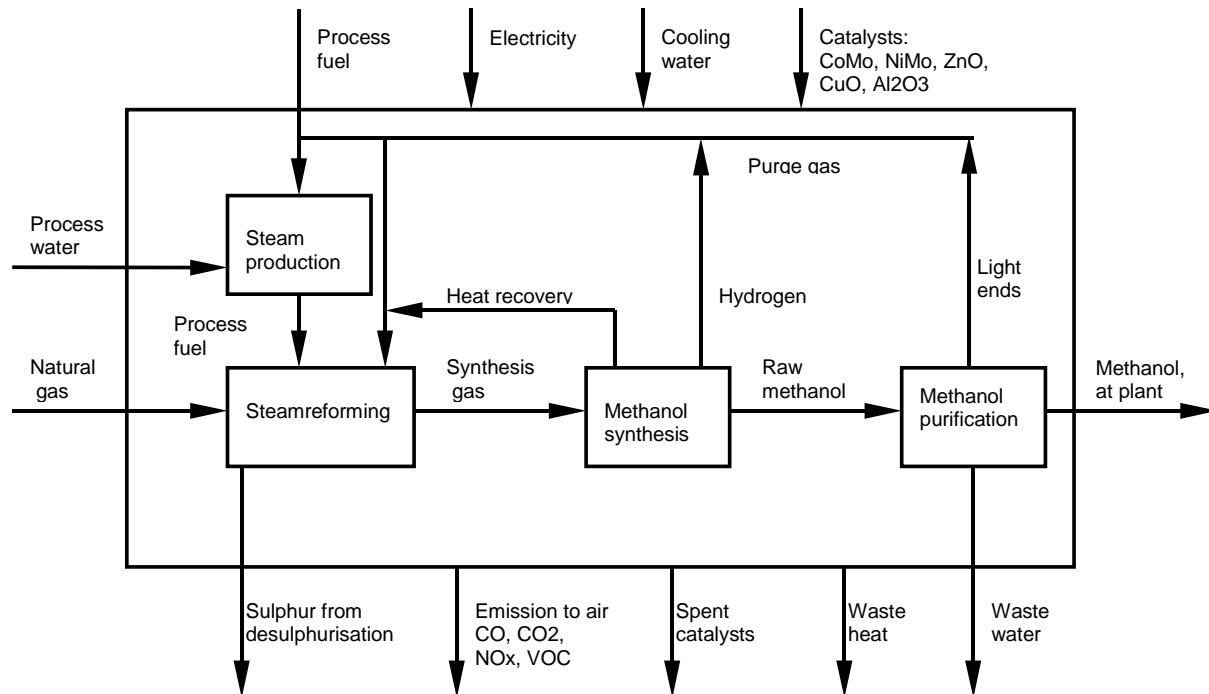


Fig. 53.4 Simplified process of methanol production with steam reforming

As methanol production is a highly integrated process with a complicated steam system, heat recovery and often also internal electricity production (out of excess steam), there were only data of the efficiency and energy consumption of the total process available. Therefore the process was not divided into a reforming process, a synthesis process and a purification process for estimating the energy and resource flows. Also the energy and resource flows in the methanol production plants are site specific (dependent on the local availability of resources such as CO₂, O₂, or electricity). In this inventory typical values for a methanol plant using steam-reforming technology were used.

53.5.2 Resources

Natural gas

The main resource for methanol production is natural gas, which acts as feedstock and fuel. A natural gas based methanol plant consumes typically 29-37 MJ (LHV) of natural gas per 1 kg of methanol. This gas is needed as feedstock for the produced methanol (20 MJ kg⁻¹ LHV) and also used as fuel for the utilities of the plant. The values selected for this inventory are given in Tab. 53.5.

In order to assess the average natural gas consumption and to show the range of the consumption depending on the technology used, data to three different process types were collected. In Tab. 53.2 values for the steam reforming processes are presented. This process is still the most common, but will be of lower importance for new methanol plants. The highest natural gas consumption show older methanol plants using steam reforming. Most of these plants will be revamped or shut down due to economic reasons. A typical total natural gas demand for the steam reforming process is around 33 MJ kg⁻¹ methanol (LHV). This value is split into a share of feed, which is mainly converted to methanol and a share of fuel, which is directly burned in the reformer furnace.

Tab. 53.2 Natural gas demand for methanol production with steam reforming. Detailed plant data.

Plant size	Gas demand (LHV) per kg methanol			Gas demand (HHV) per kg methanol		
	Total	Feed	Fuel	Total	Feed	Fuel
	MJ	MJ	MJ	MJ	MJ	MJ
2500 t d ⁻¹ , ¹	33.2	30.4	2.8	36.8	33.7	3.1
2000 t d ⁻¹ , ²	32.3	31.0	1.3	35.8	34.4	1.4
2500 t d ⁻¹ , ³	34.3	31.7	2.6	38.0	35.1	2.9
500 t d ⁻¹ , ⁴	35.4 (36.7)	-	-	39.2 (40.7)	-	-
Unspecified, ⁵	33.5	-	-	37.2	-	-

Conversion from net calorific value (LHV) to gross calorific value (HHV) with Factor 1.11 (for natural gas).

¹ Source: (Le Blanc et al. 1994), p. 92.

² Source: (Nitrogen 1995), p. 51. Source is a Foster Wheeler study cited in this article.

³ Typical values based on a moderate efficiency ICI LPM Process (Fitzpatrick 2000).

⁴ Source: (Fritsch 2000). Values of a revamped ICI LP methanol process plant built in 1972. Values in brackets before revamping.

⁵ Typical process efficiencies and utility consumption derived from other studies (Synetix 2000b).

The total natural gas demand for methanol production with combined reforming given by Le Blanc et al. 1994 (p. 92) seems to have a high value compared to the values of feed or fuel (utilities) of the same study (see Tab. 53.3). More appropriate to the other references would be the calculated sum of feed and fuel per kg methanol of 28.4 MJ kg⁻¹ (LHV) or 31.6 MJ kg⁻¹ (HHV). Also data of a new plant as presented in Pehnt 2002 lies with a total energy demand of 30.9 MJ kg⁻¹ (LHV) in the same rage. The energy demand of oxygen production (0.4 kg Oxygen per kg methanol produced with air separation) is also included in the values given by the other references.

Tab. 53.3 Natural gas demand for methanol production with combined reforming. Detailed plant data.

Plant size	Gas demand (LHV) per kg methanol			Gas demand (HHV) per kg methanol		
	Total	Feed	Fuel	Total	Feed	Fuel
	MJ	MJ	MJ	MJ	MJ	MJ
2500 t d ⁻¹ , ¹	32.5	26.5	1.9 (6.0)	36.1	29.5	2.1 (6.6)
2000 t d ⁻¹ , ²	29.7	28.7	1.0	33.0	31.9	1.1
2000 t d ⁻¹ , ³	28.5	-	-	31.6	-	-
Unspecified, ⁴	29.5	-	-	32.7	-	-

Conversion from net calorific value (LHV) to gross calorific value (HHV) with Factor 1.11 (for natural gas).

¹ Source: (Le Blanc et al. 1994), p. 92. Values in brackets are calculated out of difference between total demand and demand for feed.

² Source: (Nitrogen 1995), p. 51. Source is a Foster Wheeler study cited in this article.

³ Source: (Nitrogen & Methanol 2001), p. 28, Table 1.

⁴ Source: (Synetix 2000b), Typical process efficiencies and utility consumption derived from other studies.

For very large methanol plants autothermal reforming is used. The characteristic of this process type is that no fuel for a reformer is needed. On the other hand the amount for feed is higher than in the com-

bined reforming process. In total (fuel + feed) the efficiency of the autothermal reforming is similar to the combined reforming. In newly new built plants the demand of natural gas is less than 30 MJ kg⁻¹ (LHV). In Tab. 53.4 values for the autothermal reforming processes are presented.

Tab. 53.4 Natural gas demand for methanol production with autothermal reforming. Detailed plant data.

Plant size	Gas demand (LHV) per kg methanol			Gas demand (HHV) per kg methanol		
	Total	Feed	Fuel	Total	Feed	Fuel
	MJ	MJ	MJ	MJ	MJ	MJ
2000 t d ⁻¹ , ¹	31.8	31.8	0	35.3	35.3	0
5000 t d ⁻¹ , ²	28.5	-	-	31.6	-	-
Unspecified, ³	28.9	-	-	32.1	-	-

Conversion from net calorific value (LHV) to gross calorific value (HHV) with Factor 1.11 (for natural gas).

¹ Source: (Nitrogen 1995), p. 51. Source is a Foster Wheeler study cited in this article.

² Source: (Nitrogen & Methanol 2001), p. 28, Table 1.

³ Source: (Hydrocarbon Processing 1985), p. 146., MGC/MHI low pressure process (Mitsubishi 2-step reforming process).

From the different sources and process types the average value and the range used in this inventory were derived. The values selected for this inventory are given in Tab. 53.5. The high and low values presented in Tab. 53.5 are used for the uncertainty assessment.

The values presented by Le Blanc et al. 1994 (p. 123) were taken as average for the total natural gas consumption. These values were derived from a typical methanol plant (750'000 t a⁻¹). The energy consumption for feed and fuel were calculated from this value with the same ratio as the data presented in Fitzpatrick 2000 which represent a moderate efficiency ICI LPM Process. The demand of externally produced electricity is not included in these values. The energy demand for the utilities (fuel) varies largely, because it is strongly dependent on the plant design. The used values base on a typical plant design.

Tab. 53.5 Natural gas demand for methanol production. Overview of the plant consumption for feed and fuel.

Value	Gas demand (LHV) per kg methanol			Gas demand (HHV) per kg methanol		
	Total	Feed	Fuel	Total	Feed	Fuel
	MJ	MJ	MJ	MJ	MJ	MJ
Average ¹	32.7	30.2	2.5	36.3	33.5	2.8
High value ²	36.7	33.9	2.8	40.7	37.6	3.1
Low value ³	28.5	27.5	1.0	31.6	30.5	1.1

Conversion from net calorific value (LHV) to gross calorific value (HHV) with Factor 1.11 (for natural gas).

¹ Source: (Le Blanc et al. 1994), p. 123. Total natural gas consumption for a typical methanol plant (750'000 t a⁻¹). Consumption for feed and fuel calculated with the same ratio as in data of (Fitzpatrick 2000) which represent values based on a moderate efficiency ICI LPM Process.

² Data from (Fritsch 2000). Total gas demand of a ICI LP plant built in 1972 before revamping. Consumption for feed and fuel calculated with the same ratio as in the average case.

³ Data from (Nitrogen & Methanol 2001), p. 28, Table 1, which represents the actual state of the art. Consumption for feed and fuel calculated with the ratio shown in the data of (Nitrogen 1995).

The data given by Fritsch 2000 were considered as maximal values for the total gas demand,. These values stem from an ICI LP plant built in 1972, before revamping to higher efficiency due to economic reasons. It can therefore be assumed that this value represents the upper limit of natural gas demand. Consumption of feed and fuel were calculated with the same ratio as in the average case.

As minimal values for the total gas demand, data given by Nitrogen & Methanol 2001 (p. 28, Table 1) were used. These values refer to a modern high efficiency combined reforming plant design as it is

used in the actually built plants in remote locations. Consumption for feed and fuel were calculated with the ratio shown in the data of Nitrogen 1995 which considers the special needs in design of combined reformer plants. In these values the electricity demand of the oxygen production (air separation) is included. Electricity is normally generated within the plant from excess steam.

To calculate the emissions it was necessary to separate the part of the feed, which is burned in the furnace (purge) from the feed, which is converted to methanol. The theoretical energy required to convert pure methane to methanol is 25 MJ per kg methanol (Le Blanc et al. 1994). The assumption that 100% of the feed is methane leads to an overestimation of the feedstock demand because the higher hydrocarbons require less theoretical energy to be converted to methanol (ethane e.g.: 22.3 MJ kg⁻¹). The error in the assumed value of 25 MJ per kg methanol was considered to be negligible. The calculated process inputs for converted feed and burned feed and fuel are shown in Tab. 53.6.

Tab. 53.6 Process inputs for converted feed and burned feed and fuel. Values used in this Inventory

Value	Process input per kg methanol			
	Converted feed¹ (LHV)	Total fuel in furnace (LHV)	Converted feed (HHV)	Total fuel in furnace (HHV)
	MJ	MJ	MJ	MJ
Average ¹	25.0	7.7	27.7	8.6
High value ²	25.0	11.7	27.7	13.0
Low value ³	25.0	3.5	27.7	3.9

Results based on a calorific value (LHV) for methane of 50.0 MJ kg⁻¹ and a gross calorific value (HHV) of 55.3 MJ kg⁻¹. Data for average, maximum and minimum values calculated of data in Tab. 53.5.

Process input for converted feed is the following process: natural gas, high-pressure transport pipeline, delivered. Process input for total fuel in furnace is the process: natural gas, burned in industrial furnace low-NO_x >100 kW.

¹ Theoretical value for the conversion of methane to methanol according to Le Blanc et al. 1994, p. 113.

From the converted feed, 1 kg methanol and 0.06 kg hydrogen is yielded. It was assumed that the purged hydrogen was also burned in the furnace. The only emission to air considered from burning hydrogen is NO_x. The energy amount generated is not considered, because the process of the furnace is specified for natural gas as fuel. The NO_x emissions of the hydrogen burning were therefore calculated separately.

It was assumed, that the natural gas (feed and fuel) is taken only to a part from a high-pressure transport pipeline (process: natural gas, high pressure, at consumer. Location: RER). For methanol plants at remote locations this assumption would include a too long pipeline. For example, the pipeline that connects the Norwegian Tjeldbergodden methanol plant with the feedstock in the Heidrun field is only 250 km long (Nitrogen & Methanol 2000). Also plants in South America (Trinidad) or other gas producing countries do not need a long pipeline to the methanol plant. To consider this fact a share of 50% of the energy demand was assumed to be processed directly by the gas field. For this share the process "natural gas, at production onshore, DZ" was used. Concerning the conversion from Nm³ to MJ, a factor of 38 MJ / Nm³ was used.

With these assumptions, from the total gas demand of 32.7 MJ a share of 50% (16.35 MJ or 0.43 Nm³) were assessed with gas directly from the production site. From the remaining 16.35 MJ (50%) only 8.65 MJ were assessed with the module "natural gas, high pressure, at consumer, RER" and the rest (7.7 MJ) is accounted in the furnace process: "natural gas, burned in industrial furnace low-NO_x >100kW, RER". This furnace process also uses the gas from a high-pressure pipeline as gas resource.

Process water (make up boiler feed water), cooling water (make up)

The steam production for reforming and synthesis needs boiler feed water. Between 0.3 kg and 0.85 kg deionised water are needed for the make up in the steam production per kg methanol.

For cooling, about 60 kg water per kg methanol produced is circulating. The applied make up of cooling water differs depending on whether the cooling system uses cooling towers to dissipate the waste heat to the air or whether direct cooling with fresh water is applied.

If only evaporation losses from cooling towers have to be replaced, the make up of cooling water can be as small as 1.3 kg water per kg methanol. If there is direct cooling with fresh water, the make up of cooling water can reach 70 kg water per kg methanol. The values derived from different plants, technologies and sources are presented in Tab. 53.7.

Tab. 53.7 Boiler feed water and cooling water demand for methanol production plants

Technology, plant size	Process water demand per kg methanol		Cooling water demand per kg methanol	
	Make up	Circulating	Make up	Circulating
	kg	kg	kg	kg
Average, 750'000 t a ⁻¹ , ¹	0.85	-	8.16	-
Steam reforming, -, ²	1.15	-	(70)	(70)
Steam reforming, 2500 t d ⁻¹ , ³	0.8	-	50	-
Steam reforming, -, ⁴	0.63	-	-	60
Steam reforming, 2000 t d ⁻¹ , ⁵	0.96	2.7 (steam)	1.32	45
Combined reforming, -, ⁴	1.11	-	-	60
Combined reforming, -, ⁶	-	-	3.1	-
Two step reforming, -, ⁷	0.3	-	(60)	(60)

Used conversion factor for water: 1 m³ = 1000 kg.

¹ Raw material consumption for a typical methanol plant based on using natural gas (Le Blanc et al. 1994, p. 123).

² ICI low-pressure process. Unclear if amount for cooling water is circulating or make up (Hydrocarbon Processing 1985, p. 144).

³ Typical values based on a moderate efficiency ICI LPM Process (Fitzpatrick 2000).

⁴ Typical utility consumption derived from other studies for the Low Pressure Methanol Process (LPM, steam reforming) and the Leading Concept Methanol (LCM, combined reforming) Technology (Synetix 2000b).

⁵ Conventional methanol plant with cooling towers (Dark & Grundy 1995, p. 27-38).

⁶ Lurgi low pressure process, combined reforming (Hydrocarbon Processing 1985, p. 145).

⁷ MGC/MHI low pressure process (Mitsubishi 2-step reforming process). Unclear if amount for cooling water is circulating or make up (Hydrocarbon Processing 1985, p. 146).

The average value and the range used in this inventory were derived from the different sources and process types. The selected values for this inventory are given in Tab. 53.8. The average value selected for this inventory represents a steam reforming process using 0.85 kg deionised water per kg methanol for the process water demand. For the cooling water demand, as average a value of 8.2 kg water per kg methanol as presented in Le Blanc et al. 1994 (p. 123) seemed reasonable. As resource “water, cooling unspecified” is used because the origin of the water is unknown and depends on the location of the plant. The high and low values presented in Tab. 53.8 are used for the uncertainty assessment.

Tab. 53.8 Water demand for methanol production. Selected values for this inventory

Values	Process water demand per kg methanol		Cooling water demand per kg methanol	
	Make up	Circulating	Make up	Circulating
	kg	kg	kg	kg
Average ¹	0.85	2.7 (steam)	8.16	60
High value ²	1.15	-	70	70
Low value ³	0.3	-	1.32	45

Used conversion factor for water: $1 \text{ m}^3 = 1000 \text{ kg}$.

¹ For typical methanol plant based on using natural gas (Le Blanc et al. 1994) For circulating cooling water data from Synetix 2000b used.

² It was assumed that there is no recycling of cooling water. Otherwise maximum data from Tab. 53.8 used.

³ Minimal data from Tab. 53.7 used.

Electricity

Electricity is used for rotary machines as compressors, fans and pumps. Most plants generated a large part of the used electricity with generators within the steam system. External electricity demand refers to additional demand from an external source (besides the internally generated electricity). Only a small amount of electricity is used from external sources. This electricity is not included in the energy for feed and fuel and has therefore to be considered as an input.

The demanded external electricity can vary largely due to the plant design. Thus, the determination of an average amount is difficult. The value given in Le Blanc et al. 1994 (p. 123) for the electricity consumption of a typical $750'000 \text{ t a}^{-1}$ methanol plant based on natural gas as feedstock was taken as average for this inventory. External electricity demand refers to additional electricity demand from an external source (besides the internally generated electricity). The selected values for this inventory are given in Tab. 53.9.

For the evaluation of a maximum and minimum value there was no data available. It can be assumed that the minimum value can be 0 kWh per kg methanol in case of a process with internal electricity production. A maximum value is reached when no electricity is produced internally and the total of 0.432 kWh per kg methanol is produced externally. In this case the internal energy demand for fuel should also be lower (by similar total efficiency).

Tab. 53.9 Electricity demand for methanol production. Selected values for this inventory

Value	External electricity demand per kg methanol		Total electricity demand per kg methanol	
	kWh	MJ	kWh	MJ
Average for this inventory, ¹	0.074	0.27	Not applica-ble	Not applica-ble
Average, $750'000 \text{ t a}^{-1}$, ¹	0.074	0.27	-	-
Steam reforming, ²	0.035	0.13	-	-
Two step reforming, ³	0	0	-	-
Power for rotating machinery, ⁴	-	-	0.432	1.56

External electricity demand refers to additional electricity demand from an external source (besides the internally generated electricity).

¹ Electricity consumption for a typical methanol plant ($750'000 \text{ t a}^{-1}$) using natural gas (Le Blanc et al. 1994, p. 123).

² ICI low-pressure process (Hydrocarbon Processing 1985, p. 144).

³ MGC/MHI low pressure process (Mitsubishi 2-step reforming process (Hydrocarbon Processing 1985, p. 146).

⁴ Total electricity demand for a conventional methanol plant with cooling towers (Dark & Grundy 1995, p. 27-38).

Catalysts

Catalysts used in methanol synthesis plants are mainly based on copper, zinc, aluminium and molybdenum obtained as metal hydroxycarbonates, which are dried and calcinated ($300 - 500^\circ\text{C}$) to convert them into finely divided metal oxide (Ullmann 2001, Chapter 4). The typical main composition (in weight %) of the catalysts for the different process steps can be given as follows:

- Desulphurisation: 4% NiO, 14% MoO₃, balance Al₂O₃, bulk density 600 kg m^{-3}
- Steam reforming: 16% NiO, balance Al₂O₃, bulk density 900 kg m^{-3}
- Methanol synthesis: 64% CuO, 24% ZnO, balance Al₂O₃, bulk density 1300 kg m^{-3}

For the synthesis process, data of the needed catalyst volume per kg produced methanol are given in Le Blanc et al. 1994 (p. 73). Depending on the converter type, the catalyst yield-factor ranges from $350 \text{ kg methanol h}^{-1} \text{ m}^{-3}$ for a quench converter up to $1000 \text{ kg methanol h}^{-1} \text{ m}^{-3}$ for an isothermal converter. The expected lifetime of the catalyst is around 2-5 years (Ullmann 2001, Chapter 4.2). Thereof the needed catalyst can be roughly estimated for the methanol synthesis process using a catalyst density of 1300 kg m^{-3} and a value of 8000 h a^{-1} production time:

- Isothermal converter, catalyst lifetime 5 years, per 1 kg methanol: 33 mg catalyst
- Quench converter, catalyst lifetime 2 years, per 1 kg methanol: 232 mg catalyst

This best case / worst case calculation shows that there is only a very small amount of catalyst needed per kg methanol. Therefore the catalyst for the synthesis process was very roughly assumed as the average of the two extremes (= 133 mg). For the desulphurisation process and the steam reforming process, the same catalyst volume was assumed. In total an amount of $4 * 10^{-4} \text{ kg catalysts}$ was accounted for the whole process. Most of this material (about 60%) is aluminium oxide (Al₂O₃) which acts as carrier. Copper oxide accounts for more than 20% of the weight. The other metal oxides were approximated with their elemental metal composition (NiO as Ni, ZnO as Zn, MoO₃ as Mn). For this inventory an amount of $2.4 * 10^{-4} \text{ kg Al}_2\text{O}_3$, $0.9 * 10^{-4} \text{ kg CuO}$, $0.2 * 10^{-4} \text{ kg Ni}$, $0.3 * 10^{-4} \text{ kg Zn}$, $0.1 * 10^{-4} \text{ kg Mo}$ were accounted.

53.5.3 Emissions

Waste heat

The total waste heat of the process is calculated as the difference between the total energy input (natural gas and electricity) minus the energy content of the methanol product (HHV). In the average case the calculation leads to a total waste heat of 13.9 MJ kg^{-1} (average case). This calculation is accurate for the assumed case that all hydrogen produced is burned in the process furnace. The waste heat from the natural gas burned in the furnace is already included in the furnace process and therefore has to be subtracted from the total amount of waste heat.

The calculated value for waste heat to be considered additionally is in the average case 5.27 MJ kg^{-1} (maximum: 6.56 MJ kg^{-1} , minimum: 5 MJ kg^{-1}). For the average case, 0.4 MJ kg^{-1} are emitted to the water and the rest (4.87 MJ kg^{-1}) to the air. The amount of waste heat into the water was calculated from the returned cooling water (6.36 kg per kg methanol) assuming a temperature increase of the water of 15°C .

Emissions to air

The emissions to the air are dominated by the emissions of the furnace. These emissions are included in the process of the furnace and therefore not discussed here. The furnace was assessed with a low-NO_x industrial furnace ($>100 \text{ kW}$).

To check the derived CO₂ emission with this assumption the CO₂ emission of the furnace were calculated with the emission factors for industrial furnace (low-NO_x, $>100 \text{ kW}$) of 56 g CO₂ per MJ (LHV)

as presented in Faist Emmenegger & Heck 2007. There were some data available of the total CO₂ emissions of different methanol plants to compare the results (see Tab. 53.10). The assumed values seemed reasonable.

To check the derived NO_x emission with this assumption, the NO_x emissions of the furnace were calculated with the emission factors for industrial furnace (low-NO_x, >100 kW) presented in Faist Emmenegger & Heck 2007. There were few data available of the total NO_x Emissions of different methanol plants to compare the results (see Tab. 53.10). These values vary within a large span. Therefore the average additional NO_x emissions of the hydrogen burnt in the furnace (not included in the furnace process because NO_x emissions are the only emissions in burning hydrogen) were also calculated with the NO_x emission factor for industrial furnace (low- NO_x, >100 kW) of 23 mg NO_x per MJ (LHV) as presented in Faist Emmenegger & Heck 2007. The burned 0.06 kg hydrogen (108 MJ kg⁻¹ H₂, LHV) was therefore assumed to lead to additional NO_x emissions of 150 mg NO_x per kg methanol produced. The maximal value was calculated from the highest NO_x emission of the plant data (steam reforming) by subtracting the maximum NO_x emissions of the furnace process. The minimal value was assumed to be zero.

NO_x emissions vary largely depending on plant design. The use of combined reforming or steam reforming with a low-NO_x burner can reduce the NO_x emissions by 70% compared to steam reforming without low-NO_x burner. The NO_x emissions for steam reforming presented by Nitrogen 1995 must be from a plant without low-NO_x burner. The actual average of the currently operated plant was assumed nearer by the values of a plant with combined reforming process. But evidently there is a lack of data to determine this value better.

Tab. 53.10 Emissions to the air for methanol production per kg methanol produced.

Substance	Methanol plant process			Values for this inventory³⁾	
	Steam reforming	Combined reforming	Autothermal reforming	Included in furnace process	Additional emissions
	kg	kg	kg	kg	kg
CO ₂	0.47 , ¹ -	0.31 , ¹	0.33 , ¹	0.431 (0.196 - 0.655)	-
NOx	0.69 *10 ⁻³ , ¹ -	0.18 *10 ⁻³ , ¹ 0.2 *10 ⁻³ , ²	0.05 *10 ⁻³ , ¹ 0.1 *10 ⁻³ , ²	0.18 *10 ⁻³ (0.08 - 0.27 *10 ⁻³)	0.15 *10 ⁻³ , ⁴ (0 - 0.42 *10 ⁻³)
SOx	-	-	-	4.2 *10 ⁻⁶ (1.9 - 6.4 *10 ⁻⁶)	13.8 *10 ⁻⁶ , ⁵
CH ₄ ⁶	0.98 *10 ⁻³			-	0.98 *10 ⁻³
CH ₃ OH ⁶	0.53 *10 ⁻³	-	-	-	0.53 *10 ⁻³

Emission values in brackets refer to minimum and maximum of calculated values.

¹ Source is a Foster Wheeler study cited in Nitrogen 1995, p. 51. 8000 h a⁻¹ plant duty assumed.

² Source: (Nitrogen & Methanol 2001), p. 28, Table 1.

³ Calculated with the emission factors for industrial furnace (low-NO_x, >100 kW) presented in Faist Emmenegger & Heck 2007 of 56 g CO₂ per MJ (LHV), 23 mg NO_x per MJ (LHV) and 0.55 mg SO₂ per MJ (LHV). Average energy input and range derived from data in Tab. 53.6.

⁴ The average value for NO_x Emissions of Hydrogen burning was calculated with the emission factor for industrial furnace (low-NO_x, >100 kW) presented in Faist Emmenegger & Heck 2007. Used energy value (LHV): 6.5 MJ kg⁻¹. The maximal value was calculated from the plant data by subtracting the NO_x emissions of the furnace process. The minimal value was assumed as zero.

⁵ Additional SO₂ emissions refer to the desulphurisation of the 25 MJ converted natural gas feed.

⁶ Emissions of purge vent and distillation vent (without emissions from reformer). Values for current steam reforming technology. NMVOC emissions accounted as CH₃OH. Source: (Unnasch et al. 2000).

In the desulphurisation unit, the sulphur content (as H₂S) in the natural gas is reduced to below 280 µg m⁻³ to prevent poisoning of the nickel catalyst in the steam reformer. There were no data available about the emissions of the regeneration of the desulphurisation unit. It was assumed that all the sulphur entering the unit is released as SO₂ during regeneration. Therefore, the emission factor of

0.55 mg SO₂ per MJ natural gas (LHV) presented in Faist Emmenegger & Heck 2007 for industrial furnaces (low-NOx, >100 kW) was applied for the total input of natural gas. Within the furnace process the SO₂ emissions are already considered. According to the values in Tab. 53.6 additional SO₂ emissions of 12.5 mg per kg methanol have to be considered for the 25 MJ converted natural gas feed.

Further VOC emissions from the purge vent and the distillation vent were considered. Data about these emissions to air were scarce. The following emission data were retrieved from Delucchi et al. 1996, Tab. 4-19: There are 0.98-0.01 g CH₄ emissions and 0.53-0.03 g NMVOC emissions reported per kg methanol. The range states the difference between current and advanced technology. For this inventory the value for the current steam reforming technology was used. 75% of the NMVOC stem from the distillation vent. From these emissions, methanol is the most probable substance emitted. For this reason all NMVOC emissions reported were accounted as methanol emissions to air in this inventory.

Emissions to water

The only regularly produced waste product that presents some difficulties is the bottoms residue obtained after distillation of pure methanol. It contains water, methanol, ethanol, higher alcohols, other oxygen-containing organic compounds, and variable amounts of paraffin (Ullmann 2001, Chapter 8). From the bottom of the refining column, 0.2 kg of polluted waste water per kg methanol is discharged (Le Blanc et al. 1994, p. 118). This water is sent to a biological treatment unit. The waterborne emissions (after treatment) are assumed as reported in Terwoert et al. 1996 (p. 122) except the BOD value because of its too low value. The BOD value used in this inventory was calculated from the amounts of methanol, formaldehyde, and phenol assuming a degradation of 96% of these substances. The quality of these emission data is unsatisfactory but because of its low importance in the total process burden no further investigations were made. The selected values for this inventory are given in Tab. 53.14.

Tab. 53.11 Emission to the water for methanol production per kg methanol produced.

Substance	Emissions from waste water ¹		Emissions from cooling water ²	
	kg per kg methanol	Concentration: g m ⁻³	kg per kg methanol	Concentration: g m ⁻³
COD	0.3 *10 ⁻³	1.5	0.19 *10 ⁻³	30
BOD	0.18 *10 ⁻³	0.9	-	-
DOC, TOC	0.18 *10 ⁻³	0.5	0.06 *10 ⁻³	10
AOX	-	-	0.001 *10 ⁻³	0.15
Phosphor (P _{tot})	-	-	0.01 *10 ⁻³	1.5
Formaldehyde, CH ₂ O	0.1 *10 ⁻³	0.5	-	-
Methanol, CH ₃ OH	0.03 *10 ⁻³	0.13	-	-
Phenol, C ₆ H ₆	0.01 *10 ⁻³	0.07	-	-
Suspended solids	0.02 *10 ⁻³	0.1	-	-
Chloride, CL ⁻	-	-	0.002 *10 ⁻³	0.3

TOC and DOC values calculated of COD value assuming DOC = TOC = 0.34 COD

¹ Source: (Terwoert et al. 1996, p. 122) except BOD value. BOD value calculated from the amounts of methanol, formaldehyde and phenol assuming a degradation of 96%. Results for concentration refer to a wastewater amount of 0.2 kg per kg of methanol produced.

² Source for the cooling water discharge from recirculating cooling water systems: (IPPC 2000, p. 206). Values refer to a cooling water discharge (blow down) of 6.36 kg per kg of methanol produced.

From the input of cooling water the not evaporated part is released again as wastewater. It is assumed that 3% of the circulating cooling water is evaporated (Dark & Grundy 1995). For the average case from the 8.16 kg of cooling water makeup per kg methanol around 1.8 kg evaporate. This means that

6.36 kg will be discharged from the cooling system. Due to the fact that chemicals were used to treat the cooling water to prevent corrosion, scaling, and fouling some pollution must be considered. The pollution was assumed to be equal to the minimum requirements for the cooling water discharge from recirculating cooling water systems as described in IPPC 2000 (p. 206). The selected values for this inventory are given in Tab. 53.14.

Emissions to soil

Emissions to the soil were not considered.

Spent catalysts

The spent catalysts contain auxiliary agents and supports, as well as copper (synthesis), nickel (gas generation), and cobalt and molybdenum (desulphurisation) as active components. These metals are generally recovered or used otherwise (Ullmann 2001, Chapter 8). For this inventory it was assumed that all catalysts would be recycled. According to the cut-off methodology of this project, no emissions were therefore accounted for the spent catalysts, their further use, or the recovering process.

53.5.4 Infrastructure

The infrastructure of the methanol plant was assessed with data from a new plant built in Siberia with a capacity of 2700 t methanol per day (Pehnt 2002). For the infrastructure demand a plant operation time of 30 years with an availability of 91% was assumed (Pehnt 2002). Thereof an amount of $37.2 * 10^{-12}$ units of the infrastructure module was calculated per kg methanol. The infrastructure of the methanol plant, containing the buildings and the equipment is discussed in Chapter 53.7.

Some plant infrastructure is already included in the furnace process (natural gas, burned in industrial furnace low-NO_x >100 kW), which represents the reformer furnace. In order not to double count this infrastructure, the infrastructure of the reformer furnace has to be subtracted from the values of the plant. With the infrastructure used for the process "natural gas, burned in industrial furnace low-NO_x >100 kW" ($2.8 * 10^{-9}$ units per MJ) as presented in Faist Emmenegger & Heck 2007 the amount to be subtracted was calculated. For this calculation an value of 7.7 MJ natural gas per kg methanol as presented in Tab. 53.6 was used. This equals to the amount of gas burned in the furnace. This amount leads to a subtraction of $21.6 * 10^{-9}$ units of the process "industrial furnace, natural gas" per kg methanol.

53.6 Methanol, at regional storage (location: CH)

53.6.1 Transportation to regional store

Methanol is traded worldwide. The recent trend toward relocating production from industrial centres to sites that are remote where inexpensive natural gas is available, has the consequence that ca. 30 % of methanol produced worldwide must be transported by sea to consumer countries (Japan, Europe, United States). Specially built tankers with capacities up to 40 000 t are available for this purpose; ships built to transport petroleum products are also used (Ullmann 2001, Chapter 6.2).

The most important European transhipment point for methanol is Rotterdam. Although production capacity in Europe ($4.1 * 10^6$ t) is not fully used (production in Europe $3.1 * 10^6$ t), it nevertheless accounts for approximately half the consumption of methanol ($5.8 * 10^6$ t in 1998) originating from other continents. European methanol production takes place in Germany, Norway, United Kingdom and the Netherlands (Delfzijl). The most important production locations, however, lie in Jose (Venezuela), Point Lisas (Trinidad) and Puntas Arenas (Chile) (RMPM 2000).

From Rotterdam methanol is distributed to inland industrial regions mainly by inland waterways on vessels with capacities up to 3000 t. Methanol is also transported in road and rail tank cars. Permanently coupled trains consisting of several large tank cars with common filling, discharge, and ventilation lines are used to supply large customers (Ullmann 2001, Chapter 6.2). The selected values for the transport requirements for the distribution of methanol to regional storage in Switzerland are given in the following table.

Tab. 53.12 Average needed transportation for distribution of 1 kg methanol to regional storage in Switzerland

Location of Plant / Vehicle	Share for CH ¹	Overseas ship	Inland ship	Rail transport	Lorry transport
	%	tkm	tkm	tkm	tkm
Continental European production	40	0	0	0.6	0.05
Norwegian production	13	1.5	0.56	0	0.05
Overseas production	47	7.5	0.56	0	0.05
Average distance	100	3.7	0.34	0.24	0.05

¹ Estimated production share of methanol consumption in Switzerland

The production share of the different plant locations used in this table was calculated as follows:

- 40% average distance, within Europe. The share of the European methanol production without Statoil plant. Calculated from Data of Nitrogen & Methanol 2000 and RMPM 2000.
- 13% overseas distance from Norway. The share of the production capacity from the Norwegian Statoil plant to European consumers was taken as a factor for the transportation share (Nitrogen & Methanol 2000).
- 47% average overseas distance, from production outside Europe (mainly large overseas methanol plants). This share of the non-European methanol according to RMPM 2000 was taken as a factor for the transportation share.

The overseas distance of the larger methanol plants to Rotterdam vary from 2500 km (Sirte, Libya) up to 13800 km (Punta Arenas, Chile). As average distance for oversea transport, the 7500 km distance from Trinidad to Rotterdam was used. The port-to-port distances were derived from Dataloy (2002).

Because the Tjelbergodden plant in Norway has an important share of the European market the 1500 km oversea distance from Trondheim to Rotterdam were taken into account separately.

The distance from Rotterdam to Basel accounts for further 560 km of inland barge tanker transport. This amount was used for all oversea transports. For regional distribution further 50 km of lorry (28 t) were added. Because most oversea methanol plants are near to a port and have pipeline connections no transport was calculated from the plant to the port.

For the average distance from plants within Europe (mainly D, NL) the transport distances were assumed to be 600 km of rail and 50 km of lorry (28 t).

53.6.2 Methanol losses during transportation and storage

Large amounts of methanol are stored in tanks that correspond in design and construction to those used for petroleum products (Ullmann 2001, Chapter 6.2). Tanks are often equipped with floating roofs but also fixed-roof tanks are used. The losses during storage and handling were estimated with data from CORINAIR 1999. The data presented there applies for the petroleum industry. For an average case, 0.5g emissions per kg product throughput were reported. The range between old and new infrastructure is 0.03-0.12 g emissions per kg product throughput. The actual emissions depend strongly on the roof type and the sealing used in the storage tanks. For this inventory the average value of 0.5 g

emissions per kg product throughput were used. The emissions were accounted as methanol emissions to air.

53.6.3 Infrastructure

The infrastructure for the regional storage of methanol was assessed using the process “liquid storage tank, chemicals, organics” with a storage capacity of 16'000 m³. For the infrastructure demand a lifetime of 50 years with an average storage time of two month was assumed for the storage tanks. This leads to an amount of $4.8 * 10^6 \text{ m}^3$ or 3.8 Mt methanol stored during the lifetime of the storage tank. Thereof an amount of $263 * 10^{-12}$ units of the infrastructure module was calculated per kg methanol.

53.7 Infrastructure, methanol plant (location: GLO)

53.7.1 Process

The infrastructure of the methanol plant was assessed using data from Pehnt 2002. In this publication a recently built methanol plant with a production capacity of 2700 t methanol per day (0.897 Mt per year) was assessed. This plant size was used for this inventory. The lifetime of the plant is accounted with 30 years. Additional 10 years were accounted for construction and dismantling of the plant (Pehnt 2002).

53.7.2 Land use

The plant assessed in Pehnt 2002 occupies a land area of 0.314 km². To receive a specific value (independent from the plant size) the land use was divided by the daily production capacity. This leads to a relative value of 0.116 m² d kg⁻¹ for this plant. From other methanol plants also the specific land use was calculated. The differences are large depending on the actual site conditions. The following values were calculated for other sites: Tjeldbergodden plant 0.593 m² d kg⁻¹ (Bently Nevada 1999), Kharg Island plant 0.120 m² d kg⁻¹ and Bandar Imam plant 0.083 m² d kg⁻¹ (Affiliated Companies 2002). As an average value for this inventory 0.16 m² d kg⁻¹ or 0.43 km² where chosen (geometric mean of the values). Further it was assumed that only 0.12 m² d kg⁻¹ or 0.323 km² (75%) are built up area. The remaining area (0.04 m² d kg⁻¹) was accounted as “industrial area, vegetation”. For the time of occupation, 30 years were assumed as plant life time (production time). Further 10 years of occupation as construction site for construction and dismantling were used (Pehnt 2002). The occupation of the area before the occupation as industrial area is not known (transformation from unknown). Depending on the actual site conditions the occupation before the erection of the plant may be as industrial area, grassland or also as barren land. There was no information available and further investigated on that subject. The calculated values for the occupation and transformation of the whole site (plant with a methanol production of 0.897 Mt per year) and per kg of product used in this inventory are given in Tab. 53.13.

53.7.3 Infrastructure

Also for the infrastructure demand a methanol plant with a production capacity of 2700 t methanol per day was used. According to Pehnt 2002 the plant was built with 4681 t unalloyed steel, 1991 t low alloyed steel 1722 t high alloyed steel, 1076 t concrete, 1022 t zinc, 430 t copper, and 37.7 t nickel.

The values used in this inventory for the material demand of the plant (including reformer furnace) are given in Tab. 53.13. For the high-alloyed steel the process “chromium steel 18/8, at plant” was used. For the unalloyed steel the process “steel, electric, at plant” was used.

To transport the materials to the plant, standard distances for Europe were applied (200 km rail, 100 km road for metals, 50 km road for concrete and 15 km road for the disposal of the concrete). Be-

cause many plants are built in remote regions, additional 1500 km sea transport (distance Rotterdam Tjeldbergodden) was accounted for 50% of the plants leading to additional 750 km sea transport in average. The sea transport was not applied for the weight of the concrete used.

There was no data available on the energy demand needed for erecting and dismantling the plant. As an estimate, the values used in the module “building, multi story” were taken. The specific value for the energy used in building machines was 4.34 MJ kg^{-1} and for electricity use 1.86 MJ kg^{-1} (per kg plant weight). For the total weight of the plant an energy demand of $47.5 * 10^6 \text{ MJ}$ as diesel in building machines and $20.4 * 10^6 \text{ MJ}$ as electricity (electricity, medium voltage, production UCTE, at grid) was calculated. These values were used in the inventory.

Tab. 53.13 Methanol plant, infrastructure demand and land use

Resource, Process	Unit	per Unit ¹	per kg of product
Steel, electric, un- and low-alloyed, at plant	kg	4.68E+06	1.74E-04
Steel, low-alloyed, at plant	kg	1.99E+06	7.40E-05
Chromium steel 18/8, at plant	kg	1.72E+06	6.40E-05
Concrete, sole plate and foundation, at plant	m ³	4.89E+02	1.82E-08
Zinc for coating, at regional storage	kg	1.02E+06	3.79E-05
Copper, at regional storage	kg	4.30E+05	1.60E-05
Nickel, 99.5%, at plant	kg	3.77E+04	1.40E-06
Diesel, burned in building machine	MJ	4.75E+07	1.77E-03
Electricity, medium voltage, production UCTE, at grid	kWh	5.66E+06	2.11E-04
Disposal, concrete, 5% water, to inert material landfill	kg	1.13E+06	4.21E-05
Transport, transoceanic freight ship, OCE	tkm	7.41E+06	2.76E-04
Transport, freight, rail, RER	tkm	1.98E+06	7.35E-05
Transport, lorry 32t, RER	tkm	1.06E+05	3.94E-05
Waste heat, to air, low population density	MJ	2.04E+07	7.58E-04
Occupation, industrial area, built up	m ² a	9.69E+06	3.60E-04
Occupation, industrial area, vegetation	m ² a	3.21E+06	1.19E-04
Occupation, construction site	m ² a	4.30E+06	1.60E-04
Transformation, from unknown	m ²	4.30E+05	1.60E-05
Transformation, to industrial area, built up	m ²	3.23E+05	1.20E-05
Transformation, to industrial area, vegetation	m ²	1.07E+06	3.98E-05

¹ Chemical plant site with a product output of 0.897 Mt a^{-1} or 26.91 Mt during the whole lifetime (30 years) of the site. Therefore, a share of $3.72 * 10^{-11}$ units of the infrastructure is needed per kg of product.

² Density used for conversion: 2200 kg m^{-3}

53.7.4 Emissions and wastes

Waste heat and emissions to air

It was assumed, that 100% of the electricity consumed or $20.4 * 10^6 \text{ MJ}$ is converted to waste heat. It was assumed that this waste heat is released to the air. Emissions from burning diesel in the building machines are considered within the module “diesel, burned in building machine”. Further emissions from erecting and dismantling the plant were not considered.

Waste processes

It was assumed that all metals are recycled and therefore no burden for disposal was included. For the concrete used in the plant the disposal process “disposal, concrete, 5% water, to inert material landfill” was applied. There were no other wastes considered.

53.8 Data quality considerations

Tab. 53.14 shows the data quality indicators for the inventory of methanol production (location GLO). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation, and sample size. The highest uncertainties exist for the water and air emission data due to missing reliable average data. The data for energy use contains some uncertainties because of the different technologies used in the plants worldwide. In general the infrastructure data (presented in Tab. 53.16) has a high uncertainty because it relies only on data of one site.

For the data of the module “methanol at regional storage” presented in Tab. 53.15 the range of values lies mainly within the distances and the modal split applied for the transportation from the production plant to the regional storage in Switzerland. The uncertainty of the applied emissions is also high but due to the low emission values it will not be of high concern.

Tab. 53.14 In- / outputs for the module “methanol, at plant”, location GLO

Process output: 1 kg, methanol, at plant, GLO						
	Name, Location	Value	Unit	Uncertainty		Comment
				Type	Score	
From technosphere	natural gas, high pressure, at consumer, RER	8.65E+0	MJ	lognorm	2,3,2,3,1,3	1.11 Data from several sources, energy split estim.
	natural gas, at production onshore, DZ	4.30E-1	Nm3	lognorm	2,3,2,3,1,3	1.11 Data from several sources, energy split estim.
	natural gas, burned in industrial furnace low-NOx >100kW	7.70E+0	MJ	lognorm	2,3,2,3,1,3	1.11 Data from several sources, energy split estim.
	electricity, medium voltage, production UCTE, at grid, UC	7.40E-2	kWh	lognorm	3,3,2,3,4,3	1.53 Data dependent on technology
	water, deionised, at plant, CH	8.50E-1	kg	lognorm	3,3,2,3,4,3	1.53 Data dependent on technology
	aluminium oxide, at plant, RER	2.40E-4	kg	lognorm	4,5,3,3,5,5	2.16 Estimated from weak data
	copper oxide, at plant, RER	9.00E-5	kg	lognorm	4,5,3,3,5,5	2.16 Estimated from weak data
	zinc for coating, at regional storage, RER	3.00E-5	kg	lognorm	4,5,3,3,5,5	2.16 Estimated from weak data
	nickel, 99.5%, at plant, GLO	2.00E-5	kg	lognorm	4,5,3,3,5,5	2.16 Estimated from weak data
	molybdenum, at regional storage, RER	1.00E-5	kg	lognorm	4,5,3,3,5,5	2.16 Estimated from weak data
Emissions	methanol plant, GLO	3.72E-11	unit	lognorm	2,3,1,3,3,5	3.10 Data from one several plants used
	industrial furnace, natural gas, RER	-2.16E-8	unit	lognorm	2,3,2,3,1,3	3.01 Calculated from natural gas in furnace
	1) Water, cooling, unspecified natural origin	8.16E-3	m3	lognorm	2,3,3,3,4,5	1.59 Data dependent on technology, average used
	Heat, waste, air, low population density	4.87E+0	MJ	lognorm	3,3,2,3,4,3	1.53 Calculated from electricity and hydrogen burned
	Nitrogen oxides, air, low population density	1.50E-4	kg	lognorm	2,3,2,3,5,4	2.25 Calculated difference, dependent on technology
	Sulfur dioxide, air, low population density	1.38E-5	kg	lognorm	2,3,2,3,5,4	2.03 Calculated difference, dependent on technology
	Methane, fossil, air, low population density	9.80E-4	kg	lognorm	2,4,1,3,4,5	1.84 Data from one source, current technology
	Methanol, air, low population density	5.30E-4	kg	lognorm	2,4,1,3,4,5	1.84 Data from one source, current technology
	Heat, waste, water, unspecified	4.00E-1	MJ	lognorm	3,3,2,3,4,3	1.80 Calculated from electricity and hydrogen burned
	COD, Chemical Oxygen Demand, water, unspecified	4.90E-4	kg	lognorm	3,5,2,3,4,5	1.89 Weak data of one source
1) Ressource	BOD5, Biological Oxygen Demand, water, unspecified	1.80E-4	kg	lognorm	3,5,2,3,4,5	1.89 Weak data of one source
	DOC, Dissolved Organic Carbon, water, unspecified	2.40E-4	kg	lognorm	3,5,2,3,4,5	1.89 Weak data of one source
	TOC, Total Organic Carbon, water, unspecified	2.40E-4	kg	lognorm	3,5,2,3,4,5	1.89 Weak data of one source
	AOX, Adsorbable Organic Halogen as Cl, water, unspecified	1.00E-6	kg	lognorm	3,5,2,3,4,5	1.89 Weak data of one source
	Formaldehyde, water, unspecified	1.00E-4	kg	lognorm	3,5,2,3,4,5	3.33 Weak data of one source
	Methanol, water, unspecified	3.00E-5	kg	lognorm	3,5,2,3,4,5	3.33 Weak data of one source
	Phenol, water, unspecified	1.00E-5	kg	lognorm	3,5,2,3,4,5	3.33 Weak data of one source
	Suspended solids, unspecified, water, unspecified	2.00E-5	kg	lognorm	3,5,2,3,4,5	1.89 Weak data of one source
	Chloride, water, unspecified	2.00E-6	kg	lognorm	3,5,2,3,4,5	1.89 Weak data of one source
	Phosphorus, water, unspecified	1.00E-5	kg	lognorm	3,5,2,3,4,5	1.89 Weak data of one source

Tab. 53.15 In- / outputs for the module “methanol, at regional storage”, location CH

Process output: 1 kg, methanol, at regional storage, CH						
	Name, Location	Value	Unit	Uncertainty		Comment
				Type	Score	
	methanol, at plant, GLO	1.00E+0	kg	lognorm	1,1,1,1,1,1	1.05 Material input, no additional uncertainty
	liquid storage tank, chemicals, organics, CH	2.63E-10	unit	lognorm	4,5,1,5,3,5	3.19 Estimated
=	transport, lorry 28t, CH	5.00E-2	tkm	lognorm	3,3,1,2,1,5	2.06 Estimate of distances for imports to Switzerland
=	transport, freight, rail, RER	2.40E-1	tkm	lognorm	3,3,1,2,1,5	2.06 Estimate of distances for imports to Switzerland
=	transport, barge tanker, RER	3.40E-1	tkm	lognorm	3,3,1,2,1,5	2.06 Estimate of distances for imports to Switzerland
=	transport, transoceanic tanker, OCE	3.70E+0	tkm	lognorm	3,3,1,2,1,5	2.06 Estimate of distances for imports to Switzerland
=	Methanol, air, low population density	5.00E-4	kg	lognorm	4,5,4,3,5,5	2.42 Weak data from fuel storage
(1) from technosphere; 2) Emissions to air						

Tab. 53.16 In- / outputs for the module “methanol plant”, location GLO

Process output: 1 unit, methanol plant, GLO						
	Name, Location	Value	Unit	Uncertainty		Comment
				Type	Score	
	electricity, medium voltage, production UCTE, at grid, UCT	5.66E+6	kWh	lognorm	4,5,1,5,4,5	1.69 Estimated from building construction
	diesel, burned in building machine, GLO	4.75E+7	MJ	lognorm	4,5,1,5,4,5	1.69 Estimated from building construction
from technosphere	zinc for coating, at regional storage, RER	1.02E+6	kg	lognorm	2,4,1,3,1,5	3.06 Data from one plant
	nickel, 99.5%, at plant, GLO	3.77E+4	kg	lognorm	2,4,1,3,1,5	3.06 Data from one plant
	steel, electric, un- and low-alloyed, at plant, RER	4.68E+6	kg	lognorm	3,4,1,3,1,5	1.26 Data from one plant, estimates
	steel, low-alloyed, at plant, RER	1.99E+6	kg	lognorm	2,4,1,3,1,5	1.24 Data from one plant
	chromium steel 18/8, at plant, RER	1.72E+6	kg	lognorm	3,4,1,3,1,5	1.26 Data from one plant, estimates
	copper, at regional storage, RER	4.30E+5	kg	lognorm	2,4,1,3,1,5	1.24 Data from one plant
	concrete, sole plate and foundation, at plant, CH	4.89E+2	m3	lognorm	2,4,1,3,1,5	1.24 Data from one plant
	disposal, concrete, 5% water, to inert material landfill, CH	1.13E+6	kg	lognorm	2,4,1,3,3,5	3.11 Data from one plant, process for CH
	transport, lorry 32t, RER	7.38E+6	tkm	lognorm	3,5,1,3,4,5	1.64 Estimated with standard distances for europe
	transport, transoceanic freight ship, OCE	5.41E+6	tkm	lognorm	3,5,1,3,4,5	1.64 Estimated according to plant location
	transport, freight, rail, RER	1.44E+6	tkm	lognorm	3,5,1,5,4,5	2.35 Estimated with standard distances for europe
	Occupation, construction site	4.30E+6	m2a	lognorm	3,4,2,3,3,5	1.65 Estimated with data from several plants
	Occupation, industrial area, built up	9.69E+6	m2a	lognorm	3,4,2,3,3,5	1.65 Estimated with data from several plants
	Occupation, industrial area, vegetation	3.21E+6	m2a	lognorm	3,4,2,3,3,5	1.65 Estimated with data from several plants
Resources	Transformation, from unknown	4.30E+5	m2	lognorm	3,4,2,3,3,5	2.12 Estimated with data from several plants
	Transformation, to industrial area, built up	3.23E+5	m2	lognorm	3,4,2,3,3,5	2.12 Estimated with data from several plants
	Transformation, to industrial area, vegetation	1.07E+5	m2	lognorm	3,4,2,3,3,5	2.12 Estimated with data from several plants
	= Heat, waste, air, low population density	1.54E+7	MJ	lognorm	4,5,1,5,4,5	1.69 Calculated from electricity demand
	(1) Emissions to air					

53.9 Cumulative results and interpretation

Results of the cumulative inventory of both datasets can be downloaded from the database.

53.10 Conclusions

The production of methanol is determined largely by the impact of the natural gas feedstock. For further work on this inventory a differentiation of the most common production processes should be done. Also detailed analysis of transport routes and distances as well as the gas sources would improve the quality of the inventory. Further improvements can be achieved if the process emissions of the furnace (especially NOx) and the data quality on water emission are further investigated.

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54 Methyl ethyl ketone

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 Review: Heiko Kunst, TU Berlin

54.1 Introduction

Methyl ethyl ketone ($\text{CH}_3\text{COCH}_2\text{CH}_3$, CAS-No. 78-93-3) is at room temperature a colourless liquid with an odour close to the odour of acetone (Neier & Strehlke (2000)). Methyl ethyl ketone is 100% miscible with most of the organic solvents while in water it is only partially miscible. For this inventory the functional unit is 1 kg liquid methyl ethyl ketone. The most important chemical and physical properties of methyl ethyl ketone used in this inventory are given here.

Synonyms for methyl ethyl ketone: MEK, 2-butanone

Tab. 54.1 Chemical and physical properties of methyl ethyl ketone (according to Neier & Strehlke (2000))

Property	Unit	Value	Remarks
Molecular weight	g mol^{-1}	72.11	
Boiling point	°C	79.6	at normal pressure
Melting point	°C	-86.9	at normal pressure

54.2 Reserves and Resources of material

The production of methyl ethyl ketone is made nowadays almost only by dehydrogenation of sec-butyl alcohol (SBA), itself a product out of n-butenes, a C₄ raffinate from petrochemical processes. Therefore, all further discussion of resources equals to the discussion about the oil reserves (see Dones et al. (2007)).

54.3 Use of material / product

According to Neier & Strehlke (2000), MEK is first of all used as an important solvent, mainly due to its quite similar properties compared with acetone. In contrast with the latter one, MEK has a very high power of dissolution, a favourable volume-mass ratio (low density) and a high miscibility with almost all types of hydrocarbons. Besides its use as solvent, MEK is used as a chemical feedstock, although there it has no importance at all.

In 1979, the worldwide production capacity of methyl ethyl ketone was in the order of 640 kt. Thereof, about 50% was situated in North America and another 25% in Western European countries. In 1995, the worldwide production was in the order of 730 kt (Neier & Strehlke (2000)).

54.4 Systems characterization

In the production process for methyl ethyl ketone the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of methyl ethyl ketone is not considered to be high. For this inventory the functional unit is 1 kg of liquid methyl ethyl ketone. As process location Europe (RER) is used.

According to neier2000, nowadays, about 90% of the worldwide production is produced out of n-butene by (i) hydration to sec-butyl alcohol and (ii) a following dehydrogenation of this alcohol. The

remaining part of MEK is produced by catalytical oxidation out of liquid butane. Due to the fact that very few data are available about the process – in this study only the first mentioned production scheme is taken further into account.

There, n-butenes is either hydrated by a catalytic two-step process or in a single-step process by direct addition of water (Neier & Strehlke (2000)). The second step – the dehydrogenation of sec-butyl alcohol – is a catalytic reaction, using usually copper, zinc or bronze as catalyst. The whole reaction takes place at a temperature of about 350 to 400°C. The different steps of the process chain are shown in the following figure. The yield of the system is between 90 and 95% - here a yield of 95% is assumed in accordance with the methodology of the whole project.

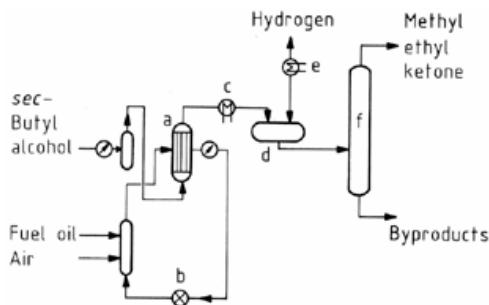


Fig. 54.1 Process chain for the production of methyl ethyl ketone by gas-phase dehydrogenation of sec-butyl alcohol (Fig.1 out of Neier & Strehlke (2000) – showing reactor [a], oil circulation heating [b], condenser [c], separator [d], refrigerator [e] and distillation [f])

54.5 Methyl ethyl ketone, at plant (Location: RER)

54.5.1 Process

This dataset includes a rough estimation of the production process for methyl ethyl ketone. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The overall reaction of the two steps – hydration of n-butene and dehydrogenation of sec-butyl alcohols - can be summarized as:



54.5.2 Resources

Energy

There was no further information available on the amount of energy used for the production process than that the second step is an endothermic reaction, using 51 kJ/mol. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the methyl ethyl ketone production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an

amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was used. A summary of the values used is given in Tab. 54.2.

Raw materials and Chemicals

According to the above shown reaction equations - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of methyl ethyl ketone:

- n-butene, C₄H₈: 776.591 g (13.868 mol)
- water, H₂O: 249.619 g (13.868 mol)

For the production a yield of 95% for the overall reaction out of n-butene is used. Therefore 817.465 g n-butene and 262.757 g water are considered as raw materials in this inventory. For the amount of process water in this study here a value of 0.25% of the cooling water amount is used. A summary of the values used is given in Tab. 54.2.

Cooling water

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the methyl ethyl ketone production.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module "chemical plant, organics" was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg methyl ethyl ketone was included.

54.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg methyl ethyl ketone is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of methyl ethyl ketone. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input as well as 0.2% of the produced hydrogen.

This assumption leads to air emissions of 1.635 g n-butenes and 0.055 g hydrogen.

Emissions to water

The remaining amount of unreacted n-butenes is assumed to leave the production process with the waste water, leading to a pollution of the waste water with 39.238 g n-butenes. Further it was assumed that all the waste water is treated in an internal waste water plant. The removal efficiency for n-butenes was assumed with 90% leading to emissions of 3.924 g n-butenes per kg product in the treated water. The carbon contained in the removed phenol was accounted as CO₂ emissions to air (110.989 g CO₂ per kg product). The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of propene in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 54.2.

Solid wastes

Solid wastes occurring during the production of methyl ethyl ketone were neglected in this inventory.

Tab. 54.2 Energy demand, Resource demand and emissions for the production of methyl ethyl ketone.

[per kg methylethylketone]			Remark
INPUTS			
n-butene	kg	0.817	stoichiometric calc., 95% yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m ³	2.40E-02	estimation
Water, process, unspecified	m ³	6.00E-03	estimation
transport by train	tkm	4.90E-01	calculated with standard distances
transport by lorry	tkm	8.17E-02	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
n-butene, to air	kg	1.64E-03	estimated as 0.2% of input
hydrogen, to air	kg	5.50E-05	estimated as 0.2% of by-product output
carbon dioxide, fossil, to air	kg	1.11E-01	from waste water treatment
n-butene, to water	kg	3.92E-03	calculated from mass balance
COD, BOD	kg	1.29E-02	calculated from water emissions
TOC, DOC	kg	3.36E-03	calculated from water emissions

54.6 Data quality considerations

The following table shows the data quality indicators for the inventory of methyl ethyl ketone production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the methyl ethyl ketone production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 54.9.

Tab. 54.3 Input / Output and uncertainty for the process “methyl ethyl ketone, at plant (RER)”

Explanation	Name	Location	Unit	methyl ethyl ketone, at plant		standardDeviation95%	GeneralComment		
				RER					
				0	kg				
Resource Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	Water, unspecified natural origin		m3	6.00E-03	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	butene, mixed, at plant	RER	kg	8.17E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation		
	transport, freight, rail	RER	tkm	4.90E-01	1	2.09	(4,5,na,na,na,na); standard distances		
Output Air emission Water emission	transport, lorry 32t	RER	tkm	8.17E-02	1	2.09	(4,5,na,na,na,na); standard distances		
	methyl ethyl ketone, at plant	RER	kg	1					
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input		
	Carbon dioxide, fossil		kg	1.11E-01	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Butene		kg	1.64E-03	1	2.32	(5,5,na,na,na,5); estimation		
	Hydrogen		kg	5.50E-05	1	2.32	(5,5,na,na,na,5); estimation		
	BOD5, Biological Oxygen Demand		kg	1.29E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	COD, Chemical Oxygen Demand		kg	1.29E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	DOC, Dissolved Organic Carbon		kg	3.36E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	TOC, Total Organic Carbon		kg	3.36E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Butene		kg	3.92E-03	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		

54.7 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

54.8 Conclusions

The inventory for methyl ethyl ketone is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if methyl ethyl ketone is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

54.9 EcoSpold Meta Information

ReferenceFunction	Name	methyl ethyl ketone, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Methylethylketon, ab
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid methyl ethyl ketone. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	78-93-3
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production of methyl ethyl ketone out of n-butene by (i) hydration to sec-butyl alcohol and (ii) a dehydrogenation of this alcohol. The overall process yield is of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

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55 Monochloroacetic acid

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55.1 Introduction

This chapter describes the production of monochloroacetic acid (MCA). This chemical is used primarily as an intermediate for the production of a large variety of chemicals.

Synonyms for monochloroacetic acid: Chloroacetic acid, chloroethanoic acid, MCA

55.2 Reserves and resources of MCA

MCA is a chlorinated organic compound. It is produced from the reaction of chlorine and acetic acid..

55.3 Characterisation of MCA

MCA ($C_2H_3O_2Cl$, CAS 179-11-8) has a molecular weight of 94.5 g/mol. MCA melts at about 57 °C and boils at 169°C. MCA is a corrosive and toxic product. Its crystal form decomposes on heating producing toxic and corrosive gases (hydrogen chloride, phosgene). The solution in water is a strong acid, and reacts violently with bases and is corrosive (IPCS 1999). MCA can be sold as a white powder or as a 20% aqueous solution.

55.4 Production and use of MCA

In 2000, some 43'000 tonnes of MCA were produced in the US, according to (Chemical Profile). One major German plant alone produces some 60'000 tonnes annually (Knapsack Clariant plant). Major direct and indirect uses include:

- thickening agents for the food, oil, mining, personal care, and detergent industries;
- agrochemicals (e.g. the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) accounted for nearly 25% of all US uses in the year 2000)
- thermo stabilizers for PVC (via thioglycolates);
- adhesives (e.g. via CMC/CMS/cyanoacetic ester);
- surfactants (e.g. via betaines/imidazolines/ethercarboxylic acids);
- pharmaceuticals (e.g. via CAC/ phenoxyacetic acid/glycine)

[Source: (www.mca.akzonobel.com) (Chemical Profiles)]

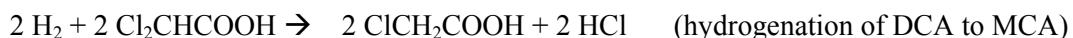
Major manufacturers include Akzo Nobel, Clariant and Dow Chemical.

55.5 System characterization

Commercial production of MCA is by direct chlorination of acetic acid or by conversion of dichloroacetic acid to MCA by hydrogen reduction. Most MCA is produced for captive use.

55.5.1 Direct chlorination of acetic acid (industry sources)

Acetic acid, mixed with 5% acetic anhydride, is fed into a reactor. Chlorine is fed into the bottom and is converted to gaseous hydrochloric acid (HCl). The HCl gas is absorbed by water to form aqueous hydrochloric acid. The product solution is distilled. The resulting crude chloroacetic acid is mixed with water, and cooled in a crystallizer to recover solid MCA. The remaining dichloroacetic acid (DCA) is removed and hydrogenated to MCA.



55.6 Life cycle Inventory for MCA

55.6.1 Precursors

Tab. 55.1 precursors per kg MCA (industry sources)

Input	kg
chlorine	0.76
Acetic acid	0.62
Acetic anhydride	0.04

According to industry sources, about 1.25 kg of HCl are obtained as a co-product per kg of MCA. As the 2000 value of chloroacetic acid was \$ 0.75 / lb and HCl was \$72 per ton, no allocation to HCl is made, as the mass x price ration is less than a 5% cut-off (Source: Chemical Profiles).

55.6.2 Energy consumption

According to Clartext 2/2002 the reaction is exothermic and the heat of reaction is fully utilized. Other sources indicate that up to 1.5 kg of steam are required per kg product. Industry sources indicate some 0.075 kWh electricity are required per kg product.

This report assumes that 0.75 kg of steam and 0.075 kWh electricity are required per kg MCA.

55.6.3 Air emissions

It is assumed that 0.2% of inputs are emitted.

Tab. 55.2 air emissions per kg MCA (assumption)

Input	kg
Chlorine	0.00152
Acetic acid	0.00124
Acetic anhydride	0.00008

55.6.4 Wastewater emissions

None given.

55.6.5 Liquid wastes

None given.

55.6.6 Solid wastes

None given.

55.6.7 Infrastructure and transports

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.0000000004 units per kg of produced monochloroacetic acid (MCA).

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

55.7 Data quality considerations

The data quality is considered to be fair, as few emissions are to be expected.

The following table summarizes the input and output data as well as the uncertainties used for the production of MCA. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 55.10.

Tab. 55.3 Input / output data and data quality for MCA production

	Name	Location	Unit	chloroacetic acid, at plant	Uncertainty Type	Standard Deviation 95%	General Comment
	Location		RER				
	Infrastructure Process		0				
	Unit		kg				
Input from Technosphere	acetic acid, 98% in H ₂ O, at plant	RER	kg	6.60E-01	1	1.12	(1,3,1,1,1,4); precursor
	chemical plant, organics	RER	unit	4.00E-10	1	1.32	(4,5,1,1,1,4); infrastructure
	chlorine, liquid, production mix, at plant	RER	kg	7.60E-01	1	1.12	(1,3,1,1,1,4); precursor
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	7.50E-02	1	1.12	(1,3,1,1,1,4); power
	heat, unspecific, in chemical plant	RER	MJ	1.80E+00	1	1.24	(4,3,1,1,1,4); steam production
	transport, freight, rail	RER	tkm	8.52E-01	1	1.24	(4,3,1,1,1,4); transport
	transport, lorry 32t	RER	tkm	1.42E-01	1	1.24	(4,3,1,1,1,4); transport
Emissions	Acetic acid	-	kg	1.32E-03	1	1.31	(4,3,1,1,1,5); air emission
	Chlorine	-	kg	1.52E-03	1	1.31	(4,3,1,1,1,5); air emission
	Heat, waste	-	MJ	2.70E-01	1	1.12	(1,3,1,1,1,4); waste heat
Outputs	chloroacetic acid, at plant	RER	kg	1			

55.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

55.9 Conclusions

The inventory for MCA is based on industry sources, estimations and assumptions. The unit process raw data are meant to be used as background information if MCA is used for a product in small

amounts. Therefore these data can give a fair approximation. They are not reliable enough for direct comparison of this material with other, alternative products

55.10 EcoSpold Meta Information

ReferenceFunction	Name	chloroacetic acid, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	All precursors and transports, as well as infrastructure.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Monochloressigsäure, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	Production of monochloroacetic acid (MCA) from the reaction of acetic acid with chlorine.
ReferenceFunction	CASNumber	79-11-8
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	RER
Technology	Text	based on literature data and plant data in Europe and North America
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	see technology
Representativeness	UncertaintyAdjustments	none

55.11 References

- Chemical Profiles Chemical profiles are published weekly in the Chemical Market Reporter, a publication of the Schnell Publishing Company, a member of the Reed Elsevier group.
- Clartext 4/2002 Hanisch, C.: "Kein Hauch von Essigduft: Monochloressigsäure aus Knapsack"
- Frischknecht et al. (2007) Frischknecht R., Althaus H.-J., Doka G., Dones R., Hischier R., Hellweg S., Jungbluth N., Kellenberger D., Nemeczek T., Rebitzer G. and Spielmann M. (2007) Overview and Methodology. Final report ecoinvent Data v2.0 No. 1. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.

56 Nitric Acid

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 Review: Heiko Kunst, TU Berlin

56.1

56.2 Introduction

Nitric acid (HNO_3 , CAS-No. 7697-37-2) is a colourless to yellow liquid with an acrid odour. It is colour fixative and an oxidising material. Nitric acid is miscible in water in all proportions. The most important chemical and physical properties are summarised in Tab 1.1.

Synonyms for Nitric Acid: Nitryl Hydroxide; Aqua fortis.

Tab. 56.1 Chemical and physical properties of nitric acid (EFMA 2000).

Property	Value	Unit	Property	Value	Unit
Molecular weight	63.0128	g mol^{-1}	Melting point	-17 (20%) -22 (60%)	°C
Density (at 20°C)	1.115 (20%) 1.367 (60%)	g cm^{-3}	Boiling point	-103.4 (20%) -120.4 (60%)	°C

The following description of production technology and the use of nitric acid are summarised from EFMA 2000, Thiemann *et al.* 1991, EMEP/CORINAIR 2001, as well as from Wiesenberger 2001.

56.3 Reserves and Resources

Nitric acid is produced basically from ammonia. Therefore, the resources available as well as the reserves are the same as for the production of ammonia, described in the corresponding Chapter.

The annual production of nitric acid in Europe was 2000 about 20 Mio tonnes 100% nitric acid (Wiesenberger 2001) and the world total production is estimated in 50 Mio tonnes (Sukalak 2002). EFMA 2000 states 78 plants in operation within the European Community in 1992, from which 45 were dual pressure plants (mostly medium p./high p.) and 33 single pressure plants (22 medium p./medium p. and 11 high pressure/high pressure). According to EMEP/CORINAIR (2001) all new plants are built for pressure ranges above 4 bar.

56.4 Production Technologies and Use

56.4.1 Production technologies for nitric acid

The production of nitric acid is based on the Ostwald Process. Initially, ammonia is oxidised catalytically. Nitrous gases are obtained, which are converted into nitric acid together with oxygen and water. All plants for the production of nitric acid are currently based on the same basic chemical operations:

- Oxidation of ammonia with air to give nitric oxide (NO)
- Oxidation of the nitric oxide to nitrogen dioxide (NO_2) and absorption in water resulting in a solution of nitric acid (HNO_3)

Two kinds of nitric acid are currently produced: weak nitric acid (50-70% acid in water) and concentrated nitric acid (about 98%).

Process technologies for weak nitric acid production differ mainly with regard to working pressure levels. There are two types of nitric acid plants, single pressure plants and dual pressure plants. In

in the single pressure plant, the oxidation and absorption takes place at the same pressure. In the dual pressure plant absorption takes place at a higher pressure than the oxidation stage. The oxidation and absorption steps can be classified according to EFMA (2000) and UNEP (1998) as:

- low pressure (below 1.7 bar)
- medium pressure (between 1.7 and 6.5 bar)
- high pressure (between 6.5 and 13 bar)

There is no concordance in the different literature sources about what should be considered low, medium and high pressures. A typical weak nitric acid plant is illustrated in Fig. 56.1, showing both the single pressure process and the additional steps from a double pressure plant.

Production of weak nitric acid: process basis

Weak nitric acid is produced by the Ostwald process. The overall reaction can be described as:



According the Ostwald process, ammonia is oxidised with air on platinum/rhodium alloy catalysts in the oxidation section of nitric acid plants. Nitric oxide and water are formed in this process according to the main equation:



Simultaneously nitrous oxide, nitrogen and water are formed as well, in accordance with the following equations:



Some of the platinum and rhodium vaporises during the reaction process and in most cases a recovery system is installed. The enthalpy of the hot reaction gases is used to produce steam and/or to preheat the waste gas. The heated waste gas is discharged to the atmosphere through a gas turbine for energy recovery. The combustion gas after this heat transfer for energy recovery has a temperature of 100 to 200 °C, depending on the process and it is then further cooled with water. The water produced in reactions (1) to (3) is then condensed in a cooler condenser and transferred to the absorption column.

The nitric oxide is oxidised to nitrogen dioxide as the combustion gases are cooled, according the equation:



For this purpose, secondary air is added to the gas mixture obtained from the ammonia oxidation to increase the oxygen content to such a level that the waste gas leaving the plant has a normal oxygen content between 2 and 4% by volume. The absorber is operated with a counter-current flow of water. The absorption of the nitrogen dioxide and the reaction to nitric acid and nitric oxide take place simultaneously in the gaseous and liquid phases according to equations (4) and (5). These reactions depend on pressure and temperature to a large extent and are favoured by high pressure and lower temperature.



Reaction (5) is exothermic and continuous cooling is therefore required within the absorber. As the conversion of NO to NO₂ is favoured by low temperature, this reaction will take place significantly

until the gases leave the absorption column. The nitric acid produced in the absorber contains dissolved nitrogen oxides and is then bleached by secondary air.

Process integrated emission reduction

Reduction facilities are normally an integral part of nitric acid plants. The two most common techniques used in order to control NOx emissions are extended absorption with water and catalytic reduction (non-selective or selective).

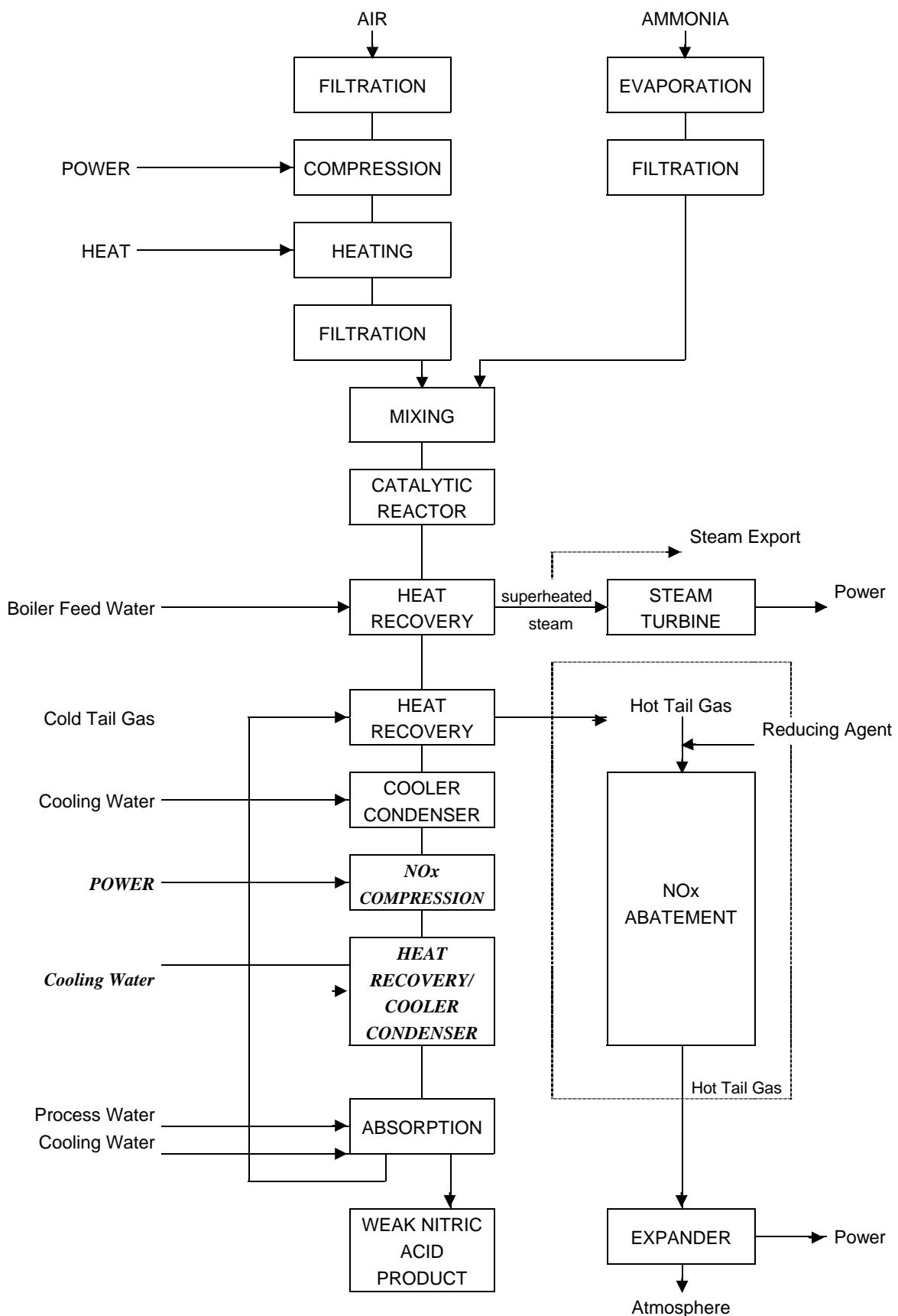
Extended absorption implies the treatment of the waste gas either with water in an additional absorption column. NOx emissions are reduced due to a better absorption efficiency.

In the non-selective catalytic reduction process the waste gas reacts with a reduction agent (hydrogen and/or hydrocarbons e.g. natural gas, waste gas from ammonia plants or naphtha) by passing through a catalyst which contains platinum, rhodium or palladium. The reduction product is N₂, however the utilisation of hydrocarbons has the disadvantage of high fuel consumption as well secondary emissions, such as CO, CO₂ and hydrocarbons in a non-converted or partially converted state. In the selective reduction process the reduction agent (ammonia) reacts with nitric oxides to form nitrogen and water. The most common catalysts used are vanadium pentoxide, platinum, iron/chromium oxides mixtures and zeolites.

Concentrated nitric acid

Weak nitric acid is also starting material in the indirect process for the production of concentrated nitric acid. This process implies the concentration of common weak nitric acid based on extractive distillation and rectification with sulphuric acid or magnesium nitrate. The other process in use for the manufacturing of concentrated nitric acid is the direct process. By this, first nitrogen dioxide (NO₂) is produced as described above for weak nitric acid. This NO₂ is then absorbed in highly concentrated acid, distilled, condensed and finally converted into highly concentrated nitric acid (about 98% w/w) at high pressure by adding a mixture of water and pure oxygen.

Fig. 56.1 Weak nitric acid production. Single pressure plant. The additional steps corresponding to the Double Pressure Process are indicated in black Italics (taken from Fig. 1 and 2 EFMA 2000)



56.4.2 Use

Nitric acid is a chemical of major industrial importance. The main use is as starting material in the production of nitrates for the fertiliser industry but it is also essential for the production of numerous other chemicals.

The most relevant use is in the manufacture of ammonium-, calcium- and potassium-nitrates. These nitrates are used as straight fertilisers or mixed into compound fertilisers. About 75 to 85% of the nitric acid produced are used in the fertiliser sector. Ammonium nitrate is also an important component of explosives. Nitric acid is also used for the digestion of crude phosphates, as nitrating agent in the preparation of explosives and organic intermediates such as nitroalkanes and nitroaromatics. It is also used in the production of adipic acid. Other applications include use as chemical in metallurgy and in rocket fuel production. Weak nitric acid is generally used in the fertiliser industry, while concentrated nitric acid is required for nitration processes.

56.5 System Characterisation

This report corresponds to the module in the ecoinvent database for the **production of 1 kg nitric acid 50% in water, at plant, in Europe**.

For this study the production of weak nitric acid with the Ostwald process is considered. According to EFMA (2000) the typical plants considered for this study are the single pressure plant and the dual pressure (medium pressure/high pressure) plant as shown in Figure 1.1. These are the processes most often used in the European industry. Except for some very old plants, single pressure plants operate at medium or high pressure and dual pressure plants operate at medium pressure for the oxidation stage and high pressure for the absorption. In literature there are different ranges for the concentration of weak nitric acid: 50-65% acid in water according to EFMA (2000), up to 69.2% to Wiesenberger (2001) and 50 to 70% according to Patyk (1997). In the database ecoinvent a concentration of 50% acid in water is considered. Nevertheless, **all data are referred to 1 kg nitric acid 100%**.

In regard to the production capacity in the manufacturing plants, EFMA (2000) considers 1000 t.d⁻¹ a typical capacity for new plants. This is the value adopted for the study. UNEP (1998) considers 1000 to 2000 t.d⁻¹ typical capacities and Wiesenberger (2001) quotes an average capacity for the Austrian plants of 660 t.d⁻¹.

The system considers the process with consumption of raw materials, energy, infrastructure and land use, as well as the generation of wastes and emissions to air and water. It also includes transportation of the raw materials and wastes. It does not include transportation of the final product nitric acid. There are no by-products generated in the production process.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage is also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to landfill.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

The relationship between the production of ammonia and nitric acid in ecoinvent is shown in the following figure.

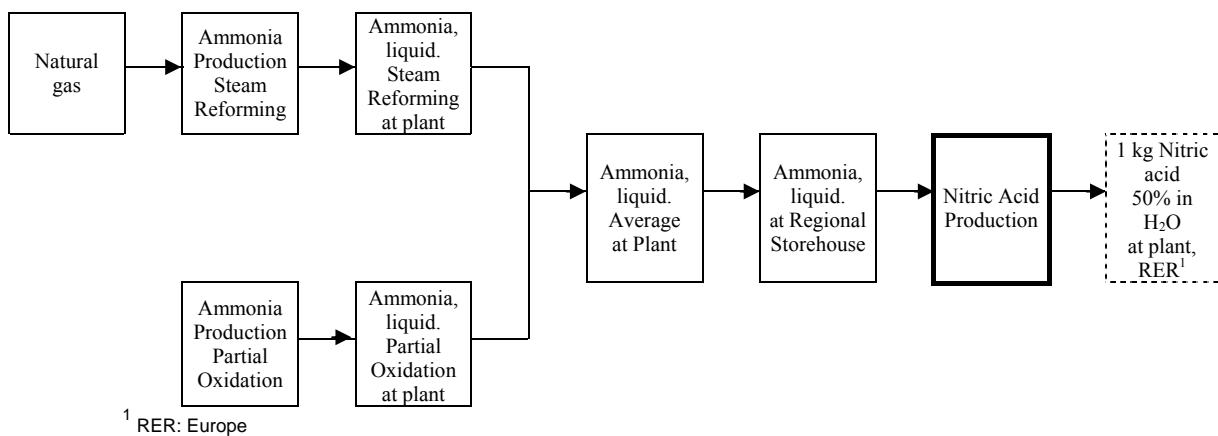


Fig. 56.2 Relationship between production of ammonia and weak nitric acid in ecoinvent

56.6 Weak Nitric Acid Production Process

56.6.1 Data sources

Main data source for this study is Patyk (1997). Wiesenberger (2001), Wiesenberger (2002)¹⁰ and EFMA (2000) and Van Balken (2002)¹¹ are also useful data sources. Additional sources (UNEP (1998), ENEP/CORINAIR (2001), Davis (1999), Kongshaug (2002) and EPA (1996)) have been taken into account for plausibility checks and comparison reasons. Wiesenberger (2003)¹² is a personal communication which apored very useful comments for this study, both on the background information on the nitric acid industry as on the emission values reported.

Patyk (1997) analyses the material flow and the energy balance of different fertilisers, considering the situation in Germany, East Europe and the EU by analysing a broad spectrum of sources, like government reports, and diverse literature. Based on these sources and on his own calculations he presents tables with values for inputs and outputs from different fertiliser production processes. The disadvantage of this very complete source is that most of the information proceed from literature and not from recent data from nitric acid plants. This survey considers evidently the burning of natural gas and heavy fuel oil for generation of energy and therefore, presents many emissions into air that are not presented in the other data sources. For this study his data referred to the EU are analysed.

Wiesenberger (2001) considers basically the actual situation for nitric acid production in Austria. The report contains data from two dual pressure plants of Agrolinz in Austria, one operating at medium pressure/high pressure and a second that operates at normal pressure/medium pressure. Data are annual average values from 1997 and 1998. Wiesenberger (2002) is a personal communication amplifying the mentioned report. The disadvantage of this highly reliable source is that it refers to only two modern production plants and therefore it is difficult to say how representative the data are for the whole European scenario. It is to be expected that the data from this source are reflecting a rather better environmental performance than the average.

EFMA (2000) is a report on the best available techniques (BAT) for nitric acid production prepared in response to the proposed EU Directive on Integrated Pollution Prevention and Control (IPPC Directive). It considers basically the state-of-the-art of nitric acid production in Europe. The document

¹⁰ Wiesenberger H. (2002) Federal Environment Agency - Austria. Personal communication on 27.09.2002

¹¹ Van Balken H. (2002) European Fertiliser Manufacturers' Association. Personal communication on 20.11.2002

¹² Wiesenberger H. (2003) Federal Environment Agency - Austria. Personal communication on 30.05.2003

represents therefore a summary of information about present state as well as future improvements possible of the weak nitric acid industry. The booklet was reviewed and updated by EFMA experts drawn from member companies. Nevertheless, no precise information about the origin of the data is available and therefore this is reflected in the uncertainty values.

Van Balken (2002) is a personal communication from a technical expert at the European Fertiliser Manufacturers Association. It supplies additional information on EFMA (2000), in regard to consumption of raw materials and energy. The origin of the data is the same as for EFMA (2000).

UNEP (1998) has the purpose of “providing guidelines”. Most of the environmental data are taken from the 1995 edition of the EFMA Report «Best Available Techniques for Pollution Prevention and Control. Production of nitric acid». The information is the consensus of the twelve West European EFMA member companies. The data remain valid (Sukalak (2002)¹³) It does not mention its other sources of information. Therefore, the values presented in this source were considered principally reference values.

Davis (1999) is a Life Cycle Inventory of Fertiliser Production from the Swedish Institute for Food and Biotechnology. In this survey, data from measures in a Swedish manufacturing plant, Hydro Agri AB in Landskrona are presented. The same as Wiesenberger (2001), this source refers to a plant with modern technology and therefore an expected environmental performance above the average. Kongshaug (1998) presents separate values for the average European plants, modern plants and older plants. He bases his observations on the database from Hydro. For this study his data referred to the average and modern plants are analysed.

EMEP/CORINAIR (2001) considers the situation in Europe. The corresponding chapter was drafted in 1995. It mainly cites sources from the early 1990s or earlier. Therefore, the values are at least 10 years old and need to be updated. They should be only taken as a rough indication of an order of magnitude (Karl (2002)¹⁴). Based on this the mentioned source is considered a rough reference.

When several values are available in the different data sources, an average is taken and the range is indicated in the form of percent variability ($\pm\%$).

56.6.2 Raw materials and auxiliaries

The most relevant raw materials for the production of nitric acid are liquid ammonia, water (mostly demineralised) and air. Platinum/rhodium alloy catalysts are also necessary for the oxidation of ammonia. Catalysts commonly used in selective reduction process are vanadium pentoxide, platinum, iron/chromium, oxides mixtures or zeolites. Wiesenberger mentions a typical catalyst composition of about 90-95% platinum and 5-10% rhodium. Other auxiliaries used in the manufacturing process are natural gas, waste gas from ammonia plants or naphtha (non-selective process) or sodium hydroxide (in the extended absorption reduction process). There is no information available about consumption of auxiliaries in the sources examined.

Tab. 56.2 gives an overview of the information about the ammonia consumption in the different sources used. There are no data available about the purity of the ammonia used as raw material. Tab. 56.3 shows the information available on water consumption. In regard to air consumption, data are available only from Wiesenberger (2001). This source mentions an input of 3.6 to 3.8 $\text{Nm}^3 \cdot \text{kg}^{-1}$ 100% HNO_3 produced.

¹³ Sukalac K. (2002) International Fertiliser Industry Association (IFA) Personal communication on 30.09.2002

¹⁴ Karl, U. (2002) French-German Institute for Environmental Research, University of Karlsruhe. Personal communication on 23.09.2002

Tab. 56.2 Liquid ammonia consumption for the production of weak nitric acid.

(kg . kg ⁻¹ 100% HNO ₃)	Van Balken 2002	Wiesenberger 2001	Patyk 1997	UNEP 1998	Davis 1999	This study
2.84 E-01 (± 1%)	2.85 E-01 (± 2%)	2.80 E-01 ¹	2.94 E-01 ² (± 12%)	2.70 E-01		2.94 E-01

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as (±%)

¹: based on Thiemann *et al.* 1991, Uhde 1993¹⁵ and Ecoinvent 1994¹⁶

²: depending on process technology

Tab. 56.3 Water consumption for the production of weak nitric acid.

m ³ H ₂ O. kg ⁻¹ 100% HNO ₃	Van Balken 2002	Wiesenberger 2001	This study
cooling water	1.30 E-01	7.20 E-02 ¹ (± 25%)	
process water	1.50 E-03	3.00 E-04 ²	
total water consumption	1.32 E-01	7.22 E-02	1.32 E-01

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as (±%)

¹ based on data from two Austrian manufacturing plants.

² based on Agrolinz (1999)¹⁷. Agrolinz Melamin GmbH. Personal communication to Wiesenberger on 12.10.1999. Corresponds to the water consumption necessary in addition to the process water arising from ammonia combustion.

The different sources report very similar values of ammonia consumption. For this study the highest value (UNEP (1998)) is used with conservative criteria, even if the corresponding source is not the main data source for this study and the value is not the newest. The reason is that while the other sources refer to state-of-the art plants, UNEP (1998) aims at reflecting the average European situation, the same as Patyk (1997). The latter reports a lower value but indicating that it may vary according to the process technology and so it does not contradict the value used. Besides, even Wiesenberger (2001), which is a state-of-the-art report, presents a higher value than Patyk (1997) and therefore for this particular input this source is not used.

In regard to water, Van Balken (2002) reports a higher overall input of water than Wiesenberger. Nevertheless, if considering the variability of the value for cooling water from the latter source, the difference between the values from both sources is not that significant. Since Van Balken (2002) reports on the average European situation and the values in Wiesenberger (2001) base on data from few manufacturing plants, the first data source is preferred in this case, also because it is the highest value available (conservative criterion).

¹⁵ Uhde GmbH (1993) Nitric Acid from Ammonia. Dortmund.

¹⁶ Baumannn *et al.* (1994) Ecoinvent – Ökoinventare für Energiesysteme: Grundlagen für den ökologischen Vergleich von Energiesystemen und den Einbezug von Energiesystemen in Ökobilanzen für die Schweiz. Im Autrag des Bundesamtes für Energiewirtschaft und des Nationalen Energie-Forschungs-Fonds NEDD, Bern.

¹⁷ Agrolinz (1999) Agrolinz Melamin GmbH. Personal communication to Wiesenberger.

56.6.3 Energy and transportation

Nitric acid production according to state-of-the-art technology is characterised by a high degree of energy recovery. Concerning the energy demand and production of the weak nitric acid production, Tab. 56.4 gives an overview of the reported energy balance in the different sources available.

Tab. 56.4 Energy inputs and outputs for the production of weak nitric acid.

Input . kg ⁻¹ 100% HNO ₃		Wiesenberger 2001	Patyk 1997	Davis 1999	Kongshaug 1998	Van Balken 2002	This study
Steam	MJ	-2.40 E+00 ¹	-2.25 E+00 ²	- 6.24 E-01	-2.42 E+00 ³ -1.55 E+00 ⁴	-1.18 E+00 ⁵ (± 30%)	-2.25 E+00
Electricity	kWh		9.00 E-03 ^{2,6}	2.66 E-01 ⁷		8.5 E-03 (± 6%)	9.00 E-03
District heating	MJ				- 2.39 ⁷		-
heavy fuel oil	MJ		9.80 E-01 ⁸				-
natural gas	MJ		8.01 E+00 ⁸				-

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as (±%) values preceded with „–“ correspond to outputs

¹ corresponding to a dual pressure plant

² based on Thiemann *et al.* 1991, Uhde 1993 and Ecoinvent 1994. Values corresponding to the EU

³ corresponding to modern plants

⁴ average for European plants

⁵ corresponding to 0.43 kg steam, assuming that 1 kg steam represents 2.75 MJ. (Boustead 1999)

⁶ UCTE mix

⁷ Swedish average

⁸ values are mentioned in Patyk (1997), but as they are from a very old source (reference year 1979!), Patyk (1997) is not using these values for further calculations

In regard to steam export, the value from Patyk (1997) is a little lower than the values from the other sources referring to state-of-the-art plants, which means no contradiction. Nevertheless, Van Balken (2002) mentions a lower value than Patyk (1997), although referring to state of the art in the European nitric acid industry. Kongshaug (1998) presents for average European plants also a lower value, what makes sense considering that very different technologies are in use for the production of nitric acid in Europe. Here in this study Patyk (1997) is used. Davis (1999) gives other values for steam export because in the manufacturing plant considered there is another export of energy, as district heating.

Concerning transportation of raw materials and auxiliaries, no information about distances is available in the examined data sources. Accordingly to the sources used, frequently a preceding ammonia plant supplies ammonia for the production of nitric acid, but there is no information about how frequent is this situation and how far are the suppliers in other cases. Therefore, for this study, it is assumed that the majority of the plants are close to their respective ammonia supplier. In Frischknecht *et al.* (1996) (Appendix A, p.19), a transport distance of 80 km on the road is assumed for the supply of a chlorine production site. Due to a lack of other information, we use for this study this value of 80 km by lorry.

Tab. 56.5 summarises the total transport amounts for the production of 1 kg of 100% nitric acid.

Tab. 56.5 Total transport distances and means for the production of weak nitric acid.

(tkm. kg ⁻¹ 100% HNO ₃)	lorry	train
raw material	2.35 E-02	0
auxiliaries	nd	nd
waste to disposal sites	nd	nd
Total transports	2.35 E-02	0

nd: no data available

56.6.4 Infrastructure and land-use

There is no information available about infrastructure and land-use of nitric acid plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. This estimated value is 4.00 E-10 unit. kg⁻¹ chemical.

56.6.5 Emissions to air and water

Most literature mentions NOx and N₂O as the relevant emissions to air in the nitric acid production. EMEP/CORINAIR (2001) mentions also emissions of ammonia (NH₃), non-methane volatile organic compounds (NMVOC) and carbon monoxide (CO) but they consider the two firsts of less relevance and the latter as not relevant. No values for the mentioned emissions are reported.

In regard to emissions to water, Patyk (1997) reports values for the emission of total nitrogen. Wiesenberger (2001) mentions non-continuous wastewater streams arising from periodical blow-downs, but no values are reported. However these streams are considered rather small.

Available information about emissions to air and water is summarised in Tab. 56.6.

Tab. 56.6 Emissions to air and water of the production of weak nitric acid.

(kg.kg ⁻¹ 100% HNO ₃)	Wiesenber- ger 2001 ²	UNEP 1998	EMEP/ CORINAIR 2001	Patyk 1997	Davis 1999	Kongshaug 1998	EFMA 2000	This study
<i>Emission to air</i>								
NO _x (as NO ₂) ¹	7.70 E-04 (± 30%)	6.90 E-03 (± 90%)	7.35 E-03 ⁶ (± 110%)	4.71 E-03	1.22 E-03		1.20 E-02 ¹² (± 90%)	4.71 E-03
N ₂ O		1.60 E-03 ³	6.50 E-04 ⁷ (± 100%)					
		4.20 E-03 ⁴	3.80 E-02 ⁸ (± 100%)					
		1.04 E-02 ⁵	8.00 E-04 ⁹					
H ₂ O			1.29 E-02 (± 40%)				3.92 E-02 (± 70%)	3.92 E-02
O ₂			1.15 E-01 (± 60%)				1.16 E-01 (± 60%)	1.16 E-01
NH ₃	2.30 E-06 (± 80%)		2.50 E-03 ⁸ (± 100%)					2.50 E-03
<i>Emission to water</i>								
N-tot					1.32 E-04			1.32 E-04

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as (±%)

¹: NOx values do not include N₂O

²: data corresponding to the two production plants operating in Austria, that are dual pressure plants with NOx reduction processes. Data from 1997 and 1998

³: target value proposed for new plants

⁴: target value proposed for existing plants (not low pressure plants) adopting NOx reduction processes

⁵: target value proposed for existing low pressure plants adopting NOx reduction processes

⁶: based on CORINAIR 1992, data corresponding to French and West German plants, without no catalytical or extended absorbed control processes.

⁷: based on CORINAIR 1992, data corresponding to French and West German plants, with catalytical or extended absorbed control processes.

⁸: CORINAIR 1990 data.

⁹: based on CORINAIR 1992, French value as used for „taxe parafiscale“

¹⁰: average for European plants

¹¹: value for a modern plant

¹²: values corresponding to modern plants without pollution abatement. Original numbers are reported as ppm. Values per kg nitric acid were calculated using values for volume of tail gas produced per kg nitric acid, which are reported in the source used.

In regard to nitrogen emissions the values are very variable between the different sources and even in the same source. The first can be due to the fact that some refer to state-of-the-art plants and other to the average situation. The second can be explained with the high variability of nitrogen emissions depending on the type of control process used and the process conditions involved (EMEP/CORINAIR (2001)). The highest values for NOx and NO₂ correspond to EFMA (2000). Even if a conservative criterion is used in ecoinvent database, these values are not used for this study since they do not take into account pollution abatement. Instead, the values from Patyk (1997) are used for this study, since this source consideres the European situation. Wiesenberger (2001), also a high reliable source consideres the situation only in Austria and therefore, the values from Patyk (1997) are preferred. EPA (1996) presents values of NOx emissions for plants without emission reduction: 2.85 E-02 kg NOx (as NO₂) .kg⁻¹ 100% HNO₃ and with emission reduction: 1.22 kg E-03 NO_x (as NO₂) .kg⁻¹ 100% HNO₃ (aver-

age). For N₂O they report 5.85 E-03 kg N₂O .kg⁻¹ 100% HNO₃. These values are not in contradiction with the values used for this study. For the other emissions, the highest value is taken.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. This waste heat is reported in Mega Joules (MJ). Therefore, a conversion from kWh to MJ is necessary. According to Frischknecht et al. (2007b) and considering the electricity input of 9.00 E-03 kWh. kg⁻¹ 100% HNO₃, the value of waste heat due to electricity consumption for this study is 3.24 E-02 MJ.kg⁻¹ 100% HNO₃. Steam for export is also considered as waste heat. Both values are added.

56.6.6 Solid wastes

Wiesenberger (2001) mentions spent oxidation catalysts and catalysts recovery gauzes. Catalysts wastes consist of precious metal losses due to vaporisation or mechanical losses. Plants operating at medium or high-pressure levels usually recover precious metals, which are processed externally. A recovery rate of about 80% is common in this case. Recovery of catalysts is not common at low oxidation pressure levels, due to high-pressure losses. Basing on Wiesenberger (2001), an amount of catalyst wastes of 3.60 E-08 kg.kg⁻¹ 100% HNO₃ is taken, which corresponds to a catalyst loss of 1.80 E-07 kg.kg⁻¹ 100% HNO₃ and a recovery rate the mentioned source for different operational conditions. The recovery rate is taken also from the mentioned source, and it corresponds to the recovery rate of platinum, taking into account that this is the principal component of catalysts (90-95%) as mentioned in section 1.5.2. Nevertheless, this waste is not relevant due to its small volume and the fact that according to Wiesenberger (2001), it mostly precipitates on cold installation plants or in the acid tank (Wiesenberger (2001) quoting Johnson Matthew (2000) and Thiemann *et. al* (1991)). Thus, in this study, this waste cannot be reported as waste to any disposal and is therefore not considered. The report also mentions wastes consisting of filter materials, which can be cleaned and reused or disposed and waste oils that have to be adequately disposed. No values are presented for the latter.

UNEP (1998) states that there are no unrecovered solid wastes in nitric acid manufacture. It specifies only catalysts and catalyst deposits, which are recovered and recycled. No values are presented.

EFMA (2000) mentions lubricating oils (that are reprocessed), catalysts recovery gauzes, filter cartridges (are disposed of but can often be cleaned and re-used) and solid deposits with platinum (that can be recovered and sent to the manufacturer or a precious metal refiner for reprocessing). The report mentions also liquid wastes originated in the boiler blow-down and in the ammonia vaporiser blow-down. No values are presented. Van Balken (2002) states a catalyst loss of 8.30 E-08 kg.kg⁻¹ 100% HNO₃, in concordance with the values for catalyst loss presented in Wiesenberger (2001).

For this study, solid waste is reported as “disposal, municipal solid waste, 22.9 %water, to sanitary landfill“, due to lack of further information about the composition of the wastes mentioned. This is considered the most appropriate among the different modules available in the database.

56.7 Data Quality Considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

Most of the used data for emissions and for energy consumption are extracted from Patyk (1997). This source is a complete review of the available information based itself on qualified sources but it has disadvantage that the information summarised may be quite outdated. Besides, it is based on literature and theoretical calculations on similar processes and less on direct information from nitric acid plants.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht *et al.* (2003b) (transport) resp. the very general module of an organic chemical plant are used. The module analysed corresponds to Europe. How-

ever, the data used for this study correspond not only to whole Europe but also to the EU or Western Europe. This lack of representativeness is reflected in the uncertainty scores.

The following table summarises the input and output data as well as the uncertainties used for the production of weak nitric acid. The values are given for the production of 1 kg of 100% nitric acid.

Tab. 56.7 Input- / Output-data for the weak nitric acid production (expressed per kg 100% nitric acid produced)

Explanation	Name	Location	Unit	nitric acid, 50% in H ₂ O, at plant		UncertaintyType	StandardDeviation95%	GeneralComment
				RER	0 kg			
Resources Input from Technosphere	Water, unspecified natural origin		m ³	2.00E-3	1	1.24	(3,1,1,1,1,5); data from survey in literature (Van Balken 2002)	
	ammonia, liquid, at regional storehouse	RER	kg	2.94E-1	1	1.24	(3,1,1,1,1,5); data from survey in literature (UNEP 1998)	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	9.00E-3	1	1.34	(3,2,3,3,3,5); data from survey in literature (Patyk 1997)	
	transport, lorry 32t	RER	tkm	2.35E-2	1	2.05	(4,na,na,na,na); Standard distances	
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); Estimation	
OUTPUTS	nitric acid, 50% in H ₂ O, at plant	RER	kg	1.00E+0				
water emission	Nitrogen		kg	1.32E-4	1	1.63	(1,4,4,3,1,5); data from survey in literature (Davis 1999)	
air emission	Nitrogen oxides		kg	4.71E-3	1	1.58	(3,2,3,3,3,5); data from survey in literature (Patyk 1997)	
	Dinitrogen monoxide		kg	8.39E-3	1	1.58	(3,2,3,3,3,5); data from survey in literature (Patyk 1997)	
	Ammonia		kg	2.50E-3	1	1.63	(3,2,4,3,1,5); data from survey in literature (EMEP CORINAIR 2001)	
	Heat, waste		MJ	2.28E+0	1	1.22	(1,3,1,3,1,5); calculated, based on electricity input & surplus steam production	

56.8 Cumulative Results and Interpretation

Results of the cumulative inventory of both datasets can be downloaded from the database.

56.9 Conclusions

An average European dataset for the production of weak nitric acid for the year 2000 is established. This dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on various reports covering the European industry, based on statistics from the time horizon 1990 up to 2000. The data are thus of a good quality and can be used in a very broad context.

56.10 EcoSpold Meta Information

ReferenceFunction	Name	nitric acid, 50% in H ₂ O, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	The inventory includes the oxidation of ammonia and the absorption steps and the final dilution of the acid.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Salpetersäure, 50% in H ₂ O, ab Werk
ReferenceFunction	Synonyms	weak nitric acid
ReferenceFunction	GeneralComment	Manufacturing process starting with ammonia is considered, plus consumption of auxiliaries, energy, infrastructure and land use, as well as generation of wastes and emissions into air and water. Transport of the raw materials, auxiliaries and wastes is included, transport and storage of the final product nitric acid are not included. No byproducts or coproducts are considered. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to landfill. Average values, based on Patyk 1997 and others (see report). Inventory refers to 1 kg 100% nitric acid.
ReferenceFunction	CASNumber	7697-37-2
TimePeriod	StartDate	1990-01
TimePeriod	EndDate	2001-12
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	Values based basically on literature using data from the 1990s and on reports from 2000-2001.
Geography	Text	European average values
Technology	Text	mostly average technology (Patyk 1997) used in european weak nitric acid production plants
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	average values from the most confident data source for each input/output
Representativeness	Extrapolations	Transports based on standard distances of Ecoinvent. Infrastructure: proxy module used (chemical plant, organics)
Representativeness	UncertaintyAdjustments	none

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57 Nitrobenzene

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57.1 Introduction

This chapter describes the production of nitrobenzene. This chemical is used primarily for the production of aniline, which is used for dyestuffs.

Synonyms for nitrobenzene: nitrobenzol, oil of bitter almonds, oil of mirbane

57.2 Reserves and resources of nitrobenzene

Nitrobenzene is an organic chemical compound. It is produced primarily from benzene by nitration.

57.3 Characterisation of nitrobenzene

Nitrobenzene is a greenish-yellow crystalline solid or pale yellow oil with a bitter almond odour, hence its nickname. It is miscible with most organic solvents, but only slightly miscible with water. Its molecular weight is 123.1 g/mol Nitrobenzene melts at 5.8 °C, and boils at about 211°C. Nitrobenzene is an eye irritant and is readily absorbed by inhalation and by the skin, which can lead to organ damage and damage to the central nervous system. Nitrobenzene forms explosive mixtures with aluminium chloride, aniline and glycerin (Wells, 1999).

57.4 Production and use of nitrobenzene

European production of nitrobenzene in 1997 was 1.22 million tonnes, according to (IPPC Chemicals, 2002). In the US, slightly over one million tons of nitrobenzene was produced in 2000 according to (Hadley & McKenna, 2001). No figures are available for Asian countries. Major plants are located in Belgium, Germany, Portugal, the UK, the Czech republic, the US and Japan. US producers are Rubicon, ChemFirst, BASF Corporation and DuPont; European producers include BASF and Bayer.

According to (Wells, 1999), most of nitrobenzene consumption is used for aniline production. Smaller amounts are used for pharmaceutical intermediates and iron oxide pigments. Nitrobenzene is also used in the production of explosives. (Hadley & McKenna, 2001), (Wells 1999).

57.5 System characterization

A nitrating acid composed of 27-32 wt% nitric acid, 56-60 wt% sulphuric acid and 8-17% water is reacted with benzene. The reaction is exothermic. On completion, spent acid and nitrobenzene are removed from the reactor into a separator. The nitrobenzene is washed and distilled. The heat of reaction can be used to evaporate the formed nitrobenzene. (Wells, 1999).



Aqueous waste acid is treated with benzene to extract nitrobenzene and nitric acid. The benzene extract is used in the reactor, whereas the denitrated acid is stored in a waste acid tank for further treatment. Benzene is recovered from the waste acid by distillation. The stripped sulphuric acid can be routed to reconcentration or can be sold (EPA L&E Benzene).

57.6 Life cycle Inventory for nitrobenzene

Specific data for stand-alone nitrobenzene plants are hard to come by, as one European company that supplied information later retracted its data and another European company chose not to share its information.

57.6.1 Precursor materials

According to (Wells, 1999), the following inputs are required for 1000 kg of nitrobenzene:

Tab. 57.1 Raw material requirements per tonne of nitrobenzene (Wells, 1999)

Input	Amount (kg)
Benzene	660
Nitric acid	535
Sulphuric acid	790
Sodium carbonate	10

The yield is reported to be 95%. Residual acid is neutralized.

57.6.2 Energy consumption

The reaction of benzene with nitric and sulfuric acid is highly exothermic. According to (Wells, 1999), the heat of reaction is almost sufficient to evaporate the nitrobenzene formed. For this reason, it is assumed that no thermal energy is required for this reaction. A value for the electrical energy is not given but is assumed to be 1.2 MJ / kg product, based on a large chemical plant site in Germany producing 2.05 Mt per year (intermediates included) of different chemicals (Gendorf 2000).

57.6.3 Air emissions

A mid-nineties EPA document gives total controlled benzene emissions at nitrobenzene plants at 0.22 – 0.39 kg / tonne (EPA L&E Benzene). This report will assume that 0.31 kg benzene are emitted per tonne of product. Controlled nitrobenzene emissions are not given. As modern plants burn their vent streams, no figures are given in this report.

57.6.4 Wastewater emissions

IPPC Chemicals (2002) indicates that less than 0.1 kg COD / tonne product and 0.1 – 1.0 kg AOX / tonne of nitrobenzene are emitted. These figures are, however, pre-biological treatment, so that this report assumes a reduction efficiency of 95%, leaving 0.005 kg COD / tonne nitrobenzene and 0.0275 kg AOX / tonne nitrobenzene to be emitted. No data is available on acid treatment / neutralisation. This report assumes that the mixed spent acids are recovered and reused.

57.6.5 Liquid wastes

No information is available.

57.6.6 Solid wastes

No information is available.

57.6.7 Infrastructure and transports

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.0000000004 units per kg nitrobenzene.

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

57.7 Data quality considerations

The data quality is considered to be fair, as it is somewhat dated and is partially based on estimates. The air emission data quality is considered poor and caution must be exercised when using them.

The following table summarizes the input and output data as well as the uncertainties used for the production of nitrobenzene. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 57.10.

Tab. 57.2 Input / output data and data quality for nitrobenzene production in Europe

Explanation	Name	Location	Unit	nitrobenzene, at plant		UncertaintyType	StandardDeviation95%	GeneralComment
				RER	kg			
				Infrastructure/Process Unit				
Input from Technosphere	benzene, at plant	RER	kq	6.60E-01	1	1.57	(2,2,1,2,4,5); literature	
	chemical plant, organics	RER	unit	4.00E-10	1	1.22	(2,2,1,2,1,5); infrastructure of a typical plant	
	electricity, medium voltage, production UCTE, at grid	UCTE	KWh	3.33E-01	1	1.88	(5,5,1,3,4,5); estimation	
	nitric acid, 50% in H2O, at plant	RER	kg	5.40E-01	1	1.57	(2,2,1,2,4,5); literature	
	sulphuric acid, liquid, at plant	RER	kg	7.90E-01	1	1.22	(2,2,1,2,1,5); literature	
	transport, freight, rail	RER	tkm	1.52E+00	1	1.24	(4,3,1,1,1,4); transport	
	transport, lorry 32t	RER	tkm	2.53E-01	1	1.24	(4,3,1,1,1,4); transport	
water emission	BOD5, Biological Oxygen Demand	-	kg	5.00E-06	1	1.22	(2,3,1,2,1,5); literature	
	COD, Chemical Oxygen Demand	-	kg	5.00E-06	1	1.22	(2,3,1,2,1,5); literature	
	AOX, Adsorbable Organic Halogen as Cl	RER	kg	2.75E-05	1	1.22	(2,3,1,2,1,5); literature	
air emission	Benzene	-	kq	3.10E-04	1	1.88	(5,5,1,3,4,5); emissions, assumed	
	Heat, waste	RER	MJ	1.20E+00	1	1.12	(1,3,1,1,1,4); waste heat	
	nitrobenzene, at plant	RER	kq	1				

57.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

57.9 Conclusions

The inventory for nitrobenzene is based mainly on literature, reporting actual plant data. The dataset is in accordance with the present quality guidelines of the ecoinvent project. The data are thus of a reasonable quality and can be used in quite a broad context.

57.10 EcoSpold Meta Information

ReferenceFunction	Name	nitrobenzene, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Included are the raw material, energy and auxillaries input together with air & water emissions. Transports and infrastructure are estimated. No waste is taken into account.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Nitrobenzol, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	This inventory is based on literature that is based on actual plant throughputs and measurements. The air emissions (benzene) are taken from mid-nineties literature.
ReferenceFunction	CASNumber	98-95-3
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	Average European Values
Technology	Text	represents a current cross-section of actual plants in Europe
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	see technology and generalComments
Representativeness	UncertaintyAdjustments	none

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58 n-Paraffins

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58.1 Reserves and Resources

n-Paraffins (CAS-No. 8002-74-2) are derivates from crude oil (kerosene or gas oil) and therefore its resources are similar to the resources for oil, described in details in Dones et al. (2007). According to Franke et al. (1995), the total European capacity for the production of n-paraffins is around 800 kt per year.

Synonyms for n-paraffins: wax; paraffin waxes; poly(methylene) wax; fischer-trosch wax;

58.2 Production Technologies and Use

58.2.1 Production technologies for n-paraffins

For the production of n-paraffins, two main routes can be distinguished – both of them based on molecular sieves adsorption and yielding in a product of very high linearity (Franke et al. (1995)):

- **Liquid phase process:** In this production process, two steps can be distinguished – the feed preparation and the n-paraffin separation. In the first of these two steps, the raw material – usually kerosene – is hydrotreated for the removal of contaminants (sulphur, nitrogen), for the protection of the molecular sieves as well as the dehydrogenation catalyst. Then, in the second step, this hydrotreated cut passes a molecular sieves extraction unit with synthetic zeolites. The process there operates in a liquid phase using a continuous countercurrent adsorption-desorption procedure.
- **Vapour phase process:** In this second possibility for the production on n-paraffins, no pretreatment of kerosene is necessary. Again, molecular sieves are used but the adsorption and desorption steps are carried out separately. The so extracted n-paraffins are further treated and cleaned by dearomatization and desulphuration steps.

58.2.2 Use of n-paraffins

Detergent grade n-paraffins are mainly used as hydrocarbon intermediates for the production of n-olefins and linear alkylbenzene (LAB). Further important applications of n-paraffins are the production of chloroparaffins or of secondary alkane sulphonates (SAS). According to Franke et al. (1995) arround 85% of the consumed n-paraffins are used as intermediates within the production of detergents.

58.3 Systems characterization

In the used sources no information about the distribution between the two different production steps is available. Based on the information of the ECOSOL study from the European Surfactants Industry in Franke et al. (1995), only a cradle to gate inventory for the production of n-paraffins – starting with the extraction of raw oil – is possible. Fig. 58.1 summarizes the included process steps.

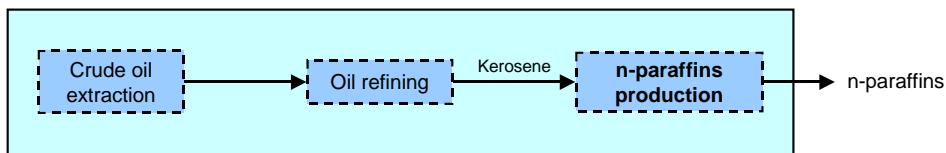


Fig. 58.1 system boundaries and flow diagramm of the production of n-paraffins out of petrochemical resources

Within the project ecoinvent, several chemical substances as well as a big party of the detergents are based on the above mentioned study from the European Surfactants Industry (summary in) Stalmans et al. (1995). Therefor, a common procedure has been established, based partly on previous work for the transformation of these data for the former detergent study of the EMPA (Dall'Acqua et al. (1999)) that is described in the following chapter.

58.3.1 Transformation from ECOSOL data into database ecoinvent

Most important point therefore is that – similar to the former detergent study of the EMPA (Dall'Acqua et al. (1999)) – the energy data have been replaced by ecoinvent specific datasets. This chapter here describes in details the applied rules and assumptions for the integration of ECOSOL data into the database ecoinvent.

Raw materials

Within the ECOSOL study, the amount of resources used is quantified in a table called "resource requirements". Thereof, only the amounts of the column "raw material" are used for this study while the amount in the second column ("energy resource") is already included into the energy input.

Auxillaries (e.g. clay, hydrogen,) are not always listed within this table, but only shown within the flow diagram of the respective processes, or mentioned within the text. Such additional auxillaries are taken into cosideration within the dataset for ecoinvent.

Energy

In Stalmans et al. (1995) there are no details of the final energy required, but only primary energy consumption reported. The final energy consumption therefore had to be estimated from the figures available and is then expressed by datasets from the database ecoinvent. The estimates made are described in detail in Tab. 58.1. Explanations of the individual columns can be found in the text below.

Tab. 58.1 Determination of thermal and electrical final energy consumption of n-paraffins (as example for the transformation of the energy values from ECOSOL to database ecoinvent)

	primary energy [GJ], total without feedstock and transports	primary energy, electrical [GJ]	in%	primary energy, thermal [GJ]	heating value [MJ/kg]	Conversion factors [kg/GJ]	thermal E., final [MJ]
nuclear	0.12	0.12	40				
hydro	0.056	0.056	19				
coal	0.51	0.07	24	0.44	28.3	71	0.22
gas	4.18	0.02	7	4.16	52.9	28.4	2.77
oil	2.70	0.03	10	2.67	44.0	33.5	1.81
total	7.566	0.3	100				
		25.83	kWh	expressed as "electricity, medium voltage, UCTE"			

expressed as "heat, at hard coal industrial furnace 1-10MW"
expressed as "heat, natural gas, at industrial furnace >100kW"
expressed as "heat, heavy fuel oil, at industrial furnace 1MW"

- *Primary energy [GJ], total without feedstock and transports:* This column lists the quantities of primary energy given in Franke et al. (1995), minus the proportion of Feedstock energy and minus the amount of transport energy (assumed to be 100% oil).

- *Primary energy, electrical [GJ]*: The fraction of nuclear energy from Franke et al. (1995) is used as a guide. The estimate is based on the assumption that nuclear energy accounts for 40% of the total electrical primary energy consumption of the processes localised to Europe. This figure accords with the UCPTE mix 1995 as reported in Dall'Acqua et al. (1999). The total electrical primary energy consumption is calculated from this. The fractions of other energy carriers for electricity production are subsequently brought closer to the UCPTE model. The percentages used are given in a separate column. From the electrical primary energy consumption in GJ we can calculate the electricity consumption required in kWh with the efficacy of the UCPTE model ($\eta = 0.31$).
- *Primary energy, thermal [GJ]*: The difference between total and electrical primary energy gives the fraction of thermal primary energy.
- *Heating value [MJ/kg]*: The heating values used in Franke et al. (1995) are calculated from the relationship between the energy used in GJ and the quantity used in kg. The values vary for different substances examined within the ECOSOL study. One reason for this is the variable fuel qualities. Another is the use of data sources with different origins.
- *Conversion factors [kg/GJ]*: The factors given in this column represent the amount of resources (raw oil, natural gas esp. coal) used for the production of 1 GJ of heat and are from Frischknecht et al. (1996). They are used to convert the thermal primary consumption into final energy consumption, expressed as "heat, from".

Transports

The total amount of transports of the different raw materials until this production step is calculated based on the reported amount of transport energy. It is assumed in this study, due to a lack of more specific information, that this transport is 100% by lorry - and therefore the transport energy is only oil. According to Spielmann et al. (2007), an average European 32t lorry needs about 37 g diesel/tkm. According to Frischknecht et al. (1996), 1 t diesel needs for the production 1.07t of raw oil. Therefore, for this study, the primary amount of oil is transformed into tkm of transport using this information together with the respective heating value for oil (calculated from the relationship between the energy used in GJ and the quantity used in kg)).

Emissions to air and water

The process emissions to air and water can be taken directly from the emissions table in the respective ECOSOL study (for n-paraffins from Franke et al. (1995)). In accordance with the methodology of this study (Frischknecht et al. (2007)), the electricity used is expressed as air emission "heat, waste". The value therefore is taken from the energy calculations described above.

All further emissions (e.g. from transports or from energy production) are included in the respective transport module esp. energy modules described above. For the transformation the parameter lists of the ECOSOL study have been adapted to the structure used in this study. All changes were made analogously to the procedure used for the transformation of the plastics data from APME (for further explications see therefore Hischier (2007)).

Tab. 58.2 gives an overview of how and with what conversion factors, the parameters from ECOSOL have been used. The conversion factors result from the relationship between the atomic weights. All parameters not given in this Table have been taken directly.

Tab. 58.2 Arrangements of parameters from ECOSOL for this study

ECOSOL name	conversion factor	ecoinvent name
<i>emission to air</i>		
particulates	0.32	particulates, > 10 um
	0.43	particulates, > 2.5 um and < 10 um
	0.25	particulates, < 2.5 um
hydrocarbons	1	both as NMVOC, non-methane volatile
other organics	1	organic compounds, unspecified data
metals	-	- (only mentioned in meta data !)
<i>emission to water</i>		
metal ion	-	- (only mentioned in meta data !)
fluorides	0.452	fluoride
phosphates as P ₂ O ₅	1.338	phosphate (PO ₄ ³⁻)
ammonia	1.06	ammonium, ion

Waste

Similar like for the emissions, the amount of process waste can be taken directly from the respective table within the ECOSOL reports. As there is no more information available about the more specific composition of this waste, it is assumed that this waste is industrial waste and - accordingly to the respective waste from APME's plastic data - is expressed by the dataset "disposal, municipal solid waste, 22.9% water, to municipal incineration" from the database ecoinvent.

Further inputs

Within ECOSOL no information is given concerning the amount of water used for process as well as for cooling. Furthermore, infrastructure is not included. Accordingly to the methodology of ecoinvent (see Frischknecht et al. (2007)) these inputs have to be included as well. Its actual inclusion is described in each case separately (e.g. n-paraffins see chapter 58.4.1).

58.4 Production of n-paraffins

58.4.1 Process data

Main source for the data is the petrochemical intermediates report from the ECOSOL study of the European LCI Surfactant Study group (Franke et al. (1995)). The data from this source have been transformed into the ecoinvent format according to the rules described above. Tab. 58.3 summarizes the resulting input and output data for the production of 1 kg of n-paraffins.

Tab. 58.3 Input and Output data for the production of 1 kg n-paraffins (data from Franke et al. (1995), transformed according to the description in chapter 58.3.1)

[per kg n-paraffins produced]			[per kg n-paraffins produced]			[per kg n-paraffins produced]		
INPUTS			OUTPUTS					
<i>raw material</i>			<i>emissions to air</i>			BOD	kg	2.00E-05
crude oil	kg	1.079	waste heat	MJ	9.30E-02	COD	kg	8.40E-05
<i>energy</i>			PM, > 10 um	kg	6.72E-05	phenol	kg	1.65E-07
electricity	kWh	2.58E-02	PM, > 2.5 um & < 10 um	kg	9.03E-05	sulphides	kg	7.71E-08
heat from heavy oil	MJ	1.81E+00	PM, < 2.5 um	kg	5.25E-05	oil	kg	1.40E-06
heat from natural gas	MJ	2.77E+00	nitrogen oxides	kg	1.72E-03	chromium	kg	2.32E-07
heat from coal	MJ	2.17E-01	NMVOC, unspecified	kg	8.20E-04	iron	kg	3.86E-07
<i>transports</i>			sulfur dioxide	kg	1.58E-03	aluminium	kg	7.71E-08
lorry, 32t	tkm	0.402	carbon monoxide, fossil	kg	4.00E-05	<td>kg</td> <td>2.32E-07</td>	kg	2.32E-07
<i>waste</i>			carbon dioxide, fossil	kg	3.11E-01	phosphates as P2O5	kg	1.61E-06
solid waste, incineration	kg	0.00492	<i>emissions to water</i>			zinc	kg	7.71E-08
			fluorides	kg	5.42E-07	ammonia	kg	2.23E-06
			suspended solids	kg	9.70E-06			

Besides these inputs and outputs, the following additional inputs are integrated into the dataset for the n-paraffins production:

- *Water, cooling water*: no information about cooling installations is given in the different sources. Nevertheless, as both processes work at high temperatures it is assumed that a cooling system exists. According to the methodology used within the different chemicals, a cooling water amount of 0.024 m³/kg product is assumed based on Gendorf (2000) (for more details see chapter of "trimethylamine" within this report !).
- *Water, process water*: no information about process water amounts is given in the different sources. Nevertheless, the emissions to water in Franke et al. (1995) shows that most of them are from the process – therefore, a process water amount of 25% of the cooling water amount is assumed.
- *Infrastructure*: As no information is given about the infrastructure, the general module for the chemicals production "chemical plant, organics" is used as a first approximation.

58.4.2 Data quality considerations

The information from Franke et al. (1995) is based on a European study and therefore representative for the average European situation. But no information is available on how much production sites these data are based on.

The resulting data together with their respective uncertainty values for the dataset „n-paraffins, at plant“ is shown in Tab. 58.4. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 58.7.

Tab. 58.4 In/Outputs and uncertainty informations for the dataset "n-paraffins, at plant"

Explanation	Name	Location	Unit	paraffin, at plant RER o kg	uncertaintyType	standardDeviation95%	GeneralComment	
							Location	InfrastructureProcess Unit
Resources	Water, cooling, unspecified natural origin	m3		2.40E-02	1	1.89	(5,5,1,5,4,5); estimated from a large chem. plant	
	Water, unspecified natural origin	m3		6.00E-03	1	1.89	(5,5,1,5,4,5); estimated from a large chem. plant	
	Oil, crude, in ground	kg		1.08E+00	1	1.31	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
Input from Technosphere	chemical plant, organics	RER	unit	4.00E-10	1	3.56	(5,5,1,5,4,5); estimated from a large chem. plant	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	2.58E-02	1	1.38	(4,5,2,1,1,5); estimation, based on ECOSOL data	
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	1.81E+00	1	1.38	(4,5,2,1,1,5); estimation, based on ECOSOL data	
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.77E+00	1	1.38	(4,5,2,1,1,5); estimation, based on ECOSOL data	
	heat, at hard coal industrial furnace 1-10MW	RER	MJ	2.17E-01	1	1.38	(4,5,2,1,1,5); estimation, based on ECOSOL data	
	transport, lorry 32t	RER	tkm	4.02E-01	1	2.1	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
Waste	disposal, municipal solid waste, 22.9% water, to municipal incineration	CH	kg	4.92E-03	1	1.31	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
Output Air emission	paraffin, at plant	RER	kg	1				
	Heat, waste		MJ	9.30E-02	1	1.31	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Particulates, > 10 um		kg	6.72E-05	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Particulates, > 2.5 um, and < 10um		kg	9.03E-05	1	2.1	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Particulates, < 2.5 um		kg	5.25E-05	1	3.1	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Nitrogen oxides		kg	1.72E-03	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	NM VOC, non-methane volatile organic compounds, unspecified origin		kg	8.20E-04	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Sulfur dioxide		kg	1.58E-03	1	1.31	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Carbon monoxide, fossil		kg	4.00E-05	1	5.11	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Carbon dioxide, fossil		kg	3.11E-01	1	1.31	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Fluoride		kg	5.42E-07	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Suspended solids, unspecified		kg	9.70E-06	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	BOD5, Biological Oxygen Demand		kg	2.00E-05	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	COD, Chemical Oxygen Demand		kg	8.40E-05	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Phenol		kg	1.65E-07	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Sulfide		kg	7.71E-08	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Oils, unspecified		kg	1.40E-06	1	3.1	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Chromium, ion		kg	2.32E-07	1	5.11	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Iron, ion		kg	3.86E-07	1	5.11	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Aluminum		kg	7.71E-08	1	5.11	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Nickel, ion		kg	2.32E-07	1	5.11	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Phosphate		kg	1.61E-06	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Zinc, ion		kg	7.71E-08	1	5.11	(2,5,2,1,1,5); data from ECOSOL study (Literature)	
	Ammonium, ion		kg	2.23E-06	1	1.62	(2,5,2,1,1,5); data from ECOSOL study (Literature)	

58.5 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

58.6 Conclusions

An average European dataset for the production of n-paraffins is established. This dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on a European detergent ingredients study, based on statistics from the first half of the 1990s. The data are nevertheless of a reasonable quality and can be used in quite a broad context.

58.7 EcoSpold Meta Information

ReferenceFunction	Name	paraffin, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	This module contains material and energy input, production of waste and emissions for the production of n-paraffins out of crude oil. Water consumption and infrastructure have been estimated.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Paraffin, ab Werk
ReferenceFunction	Synonyms	wax//Wachs
ReferenceFunction	GeneralComment	data based on the ECOSOL study of the European surfactant industry. Allocations in multioutput processes were made, using the relative mass outputs of products.
ReferenceFunction	CASNumber	
TimePeriod	StartDate	1995
TimePeriod	EndDate	1995
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	data of published literature
Geography	Text	Data based on the European paraffin production
Technology	Text	Average technology, typical for European production conditions in the mid 90s
Representativeness	Percent	
Representativeness	ProductionVolume	800 kt
Representativeness	SamplingProcedure	
Representativeness	Extrapolations	data out of ECOSOL study of European Surfactant Industry. Common translation rules used, reported in Chemical report (Althaus et al. 2003).
Representativeness	UncertaintyAdjustments	

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59 Pentaerythritol (penta, 2,2-bis(hydroxymethyl)-1,3-propanediol)

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 Review: Heiko Kunst, Berlin

59.1 Introduction

This chapter describes the production of pentaerythritol. This chemical is used primarily for the production of alkyd resins, as well as lubricants and antioxidants.

59.2 Reserves and resources of pentaerythritol

Penta is an organic chemical compound. It is produced from acetaldehyde and formaldehyde.

59.3 Characterisation of pentaerythritol

Penta consists of white crystals with a melting point of 262 °C and a boiling point 276 °C. It is flammable. When mixed with air, pentaerythritol dust is explosive at temperatures exceeding 400 °C. Pentaerythritol is miscible with boiling water, can be somewhat dissolved in alcohol and does not dissolve in benzene and other common organic solvents. (Roempp, 1991).

59.4 Production and use of pentaerythritol

Penta is produced industrially by reacting formaldehyde with acetaldehyde at 15 – 45 °C in the presence of aqueous calcium hydroxide or sodium hydroxide. Generally, a fourfold surplus of formaldehyde is used in order to minimize the production of dipentaerythritol (Roempp, 1991).

In 2002, European production of penta was approximately 130'000 tons; according to industry sources. Europe is a net exporter of penta. The following table indicates the uses and approximate shares of European consumption in 2002.

Tab. 59.1 Penta consumption in Europe in 2002 (personal communication)

Application	Share of European consumption
Alkyd resins	75%
Synthetic lubricants	10%
Rosin esters	9%
Antioxidants	4%
Pentatetranitrate for explosives	2%

59.5 System characterization

Penta is produced industrially by reacting formaldehyde with acetaldehyde. There are no competing routes for the production of penta. Production information is confidential.



59.6 Life cycle Inventory for penta

This report assumes that half of the penta is produced at a Scandinavian site and half is produced at a Western European site.

59.6.1 Precursor materials (Industry sources)

Raw materials per ton:

Formaldehyde 1040 kg

Acetaldehyde 360 kg

Caustic (50%) 750 kg

Yield: 1 ton penta, 0.63 tons sodium formate, 0.07 ton other polyols as well as 0.1 ton of a sodium formate solution. The solution is sold as a sodium and thermal energy source. The sodium formate is both sold and used captively in other processes. The mass*price ration of penta to sodium formate is approximately 9.6:1, which indicates that sodium formate, when it is sold, carries ca. 10% of the environmental burdens created during the production of penta.

59.6.2 Energy usage

8.32 MJ delivered energy. Assuming that the efficiency of fuel combustion is 70%, total fuel usage is 11.9 MJ. The steam is produced by a mix of bio- and fossil fuels.

No electrical energy is given. However, a value can be approximated from a large chemical plant site in Germany producing 2.05 Mt per year (intermediates included) of different chemicals (Gendorf 2000).. For this inventory an amount of 1.2 MJ / kg electricity was used.

59.6.3 Air emissions

There is no information on process emissions. Monitored stack missions were made available by industry sources; where these emissions had gaps, they were filled in by estimation. Starting point for the estimation of these additional emissions is the fuel mix used within the plant for the production of heat/steam.. More details about these different heating systems can be found in the respective chapters of (Dones et al. 2007). Then the resulting emissions of the different fuels are summed up and the resulting sum is used as total direct emission of the energy production

59.6.4 Wastewater emissions

According to industry sources, there are 4.3 g TOC / kg penta. This waste stream enters a wastewater treatment facility with a removal efficiency of about 92%, this amounts to 0.376 g TOC / kg penta post-treatment.

59.6.5 Liquid wastes

No liquid wastes are given.

59.6.6 Solid wastes

2.5 g process sludge per ton penta.

The wastes are usually incinerated in a company incinerator and the steam is utilized.

59.6.7 Infrastructure and transports

No information was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.0000000004 units per kg of produced penta.

Tab. 59.2 Transport of precursors (industry sources)

Precursor	Scandinavia	W. Europe
Formaldehyde	pipeline	pipeline
Acetaldehyde	Railcar 800 km	Railcar 200 km
Caustic	Railcar 200 km	Railcar 200 km

59.7 Data quality considerations

The data quality is considered to be fair, as quite a few of the air emissions reported here actually stem from monitoring. The fuels input data are in part an approximation, although the energy usage is monitored, as are the amounts of precursor substances.

The following table summarizes the input and output data as well as the uncertainties used for the production of penta.

Tab. 59.3 Input / output data and data quality for penta production in Europe

Input Category	Output Category	Name	Unit	reaction of formaldehyde with acetaldehyde	Uncertainty Type	Standard Deviation 95%	General Comment
		Location	RER				
		Infrastructure Process Unit	0				
			kg				
5	-	acetaldehyde, at plant	kg	0.36	1	1.11	,1,1,1,4); precursor
5	-	chemical plant, organics	unit	4E-10	1	1.32	,1,1,4); infrastruc
5	-	electricity, medium voltage, production UCTE, at grid	kWh	0.33	1	1.11	,1,1,1,1,4); powe
5	-	formaldehyde, production mix, at plant	kg	1.04	1	1.11	,1,1,1,4); precu
5	-	heat, heavy fuel oil, at industrial furnace 1MW	MJ	2	1	1.12	2,1,1,1,1,4); fuel
5	-	heat, natural gas, at industrial furnace >100kW	MJ	4	1	1.12	2,1,1,1,1,4); fuel
5	-	reaction of formaldehyde with acetaldehyde	kg	1	1	1.11	g to penta and c
5	-	sodium hydroxide, 50% in H ₂ O, diaphragm cell, at plant	kg	0.75	1	1.11	,1,1,1,4); precu
5	-	transport, freight, rail	tkm	0.78	1	1.15	,1,1,1,4); transp
4	-	Peat, in ground	kg	0.0174	1	1.15	,1,1,1,4); fuel
-	4	Ammonia	kg	0.0000328	1	1.11	,1,4); airborne em
-	4	Carbon dioxide, fossil	kg	0.13	1	1.15	,1,4); airborne em
-	4	Carbon monoxide, fossil	kg	1.03E-03	1	1.11	,1,4); airborne em
-	4	DOC, Dissolved Organic Carbon	kg	0.33	1	1.15	,1,4); emission to
-	4	Heat, waste	MJ	1.2	1	1.11	,1,1,1,4); waste h
-	4	Nitrogen oxides	kg	0.000659	1	1.11	,1,4); airborne em
-	4	Particulates, > 2.5 um, and < 10um	kg	0.0000387	1	1.11	,1,4); airborne em
-	4	Sulfur dioxide	kg	3.21E-04	1	1.11	,1,4); airborne em
-	4	TOC, Total Organic Carbon	kg	0.33	1	1.15	,1,4); emission to
-	2	penta-erythritol, at plant	kg	1.00E+00	1	1.11	,1,1,1,4); produc
-	2	sodium formate from the reaction of formaldehyde with acetaldehyde	kg	0.104	1	1.11	,1,1,1,4); coprod

59.8 Abbreviations

Penta. pentaerythritol

59.9 References

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60 Phenol

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60.1 Introduction

Phenol (C_6H_5OH , CAS-No. 108-95-2) is at room temperature a solid of colourless crystal prisms (jordan2000). Above its melting point, it is a clear, colourless liquid. In water phenol is only completely miscible above about 70°C. Furthermore it is soluble in most organic solvents – e.g. in alcohols, ketones, ethers as well as aliphatic or aromatic hydrocarbons. For this inventory the functional unit is 1 kg solid phenol. The most important chemical and physical properties of phenol used in this inventory are given in here.

Synonyms for phenol: hydroxybenzene, carbolic acid

Tab. 60.1 Chemical and physical properties of phenol (according to Jordan et al. (2000))

Property	Unit	Value	Remarks
Molecular weight	$g\ mol^{-1}$	94.11	
Density	$kg\ m^{-3}$	1.071	at 20°C
Boiling point	°C	181.75	at normal pressure
Melting point	°C	40.9	at normal pressure

60.2 Reserves and Resources of material

The production of phenol is made out of benzene or toluene nowadays – all of them being hydrocarbons out of oil and/or gas. Therefore, all further discussion of resources equals to the discussion about the oil / gas reserves (see Dones et al. (2007)).

60.3 Use of material / product

According to Jordan et al. (2000), the two most important uses of phenol are its function as intermediate in the production of phenol-formaldehyde resins and its use in the production of bisphenol A. The latter one is a very important intermediate for the production of e.g. epoxy resins. Besides this, other important intermediates are produced out of phenol – e.g. adipic acid or caprolactam. The latter one is getting less and less important due to the discovery of other production processes for it.

In 1995, the worldwide consumption of phenol was in the order of 5.23 Mt. Thereof, 37% was used for phenolic resins and another 32% for the bisphenol A synthesis – only the remaining rest is used for further uses (Jordan et al. (2000)).

60.4 Systems characterization

In the production process for phenol the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of phenol is not considered to be high. For this inventory the functional unit is 1 kg of solid phenol. As process location Europe (RER) is used.

According to Jordan et al. (2000), half a dozen different synthesis routes have been developed and even exploited for the production of phenol. Although, nowadays only two of these routes are of economical interest – the Hock process (production out of cumene), covering about 96% of the worldwide capacity, and the oxidation of toluene, only for about 4%. Due to the fact that the data are quite weak here, only the largely dominating Hock process is further examined here.

In this process, cumene is transformed into phenol by a two-stage process with (i) an oxidation of the cumene, and (ii) a cleavage to phenol and acetone. In the following figure, the complete process chain of the Hock process is schematically shown.

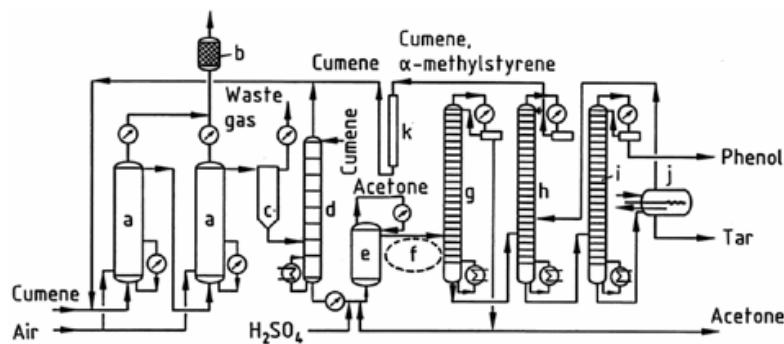


Fig. 60.1 Process chain for the production of phenol from cumene (Fig.3 out of jordan2000 – showing cumene oxidation reactor [a], waste gas purification [b], Gas seperator [c], concentration [d], cleavage reactor [e], catkayst separation [f], acetone column [g], cumene column [h], phenol column [i], cracking [j] and hydrogenation [k])

The oxidation happens in large reactors at a temperature of about 90-120°C and 0.5-0.7 MPa pressure. The whole reaction is autocatalytic and exothermic, releasing about 800 kJ per kilogram of cumene hydroperoxide to the environment by active cooling systems, mainly water.

The second reaction – the cleavage – is an acid-catalyzed reaction, using almost exclusively sulphuric acid as catalyst. Two different ways are used within industry – called homogeneous phase (using 0.1-2% sulphuric acid) resp. heterogeneous phase (40-45% sulphuric acid at a concentrate-acid ratio of 1:5). Also this second step is strongly exothermic – releasing ca. 1680 kJ per kilogram of cumene hydroperoxide cleaved.

After the cleavage, further cleaning steps are used to achieve in the end a phenol purity of >99.9%. This includes neutralization and removing of sulphuric acid, followed by distillation processes. The overall yield of the production of phenol for this case here is assumed to be in the order of 95%.

60.5 Phenol, at plant (Location: RER)

60.5.1 Process

This dataset includes a rough estimation of the production process for phenol. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The two steps described for the production of phenol can be summarized within the following reaction equation:



60.5.2 Resources

Energy

The two reactions are exothermic, releasing together about 2.6 MJ of heat per kg of cumene hydroperoxide. The further process steps of separation and purification need energy. For this study, therefore it is assumed that the whole phenol production process doesn't need any external fuel input. In order not to neglect the electricity demand of the phenol synthesis, this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). There, 38% of the 3.2 MJ kg⁻¹ of total energy consumed is electricity. Therefore, for this inventory an amount of 1.2 MJ kg⁻¹ electricity was used.

Raw materials and Chemicals

According to the above shown reaction equation - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of phenol:

- cumene, C₉H₁₂: 1275.104 g (10.626 mol)
- oxygen, O₂: 340.028 g (10.626 mol)

For the production a yield of 95% for the overall reaction out of cumene is used (see 60.4). Therefore 1342.214 g cumene and 357.924 g oxygen are considered as raw materials in this inventory. The above mentioned sulphuric acid is used as a catalyst. Assuming that the catalyst is not changed, for this study, no sulphuric acid input is taken into account here. A summary of the values used is given in Tab. 60.2.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the phenol production.

Concerning the process water consumption, no data are given. For this study here, an amount of 50% of the cooling water amount is assumed – leading to an input of 12kg water per kg phenol.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007b) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of 4 * 10⁻¹⁰ units per kg phenol was included.

60.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg phenol is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of phenol. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input.

This assumption leads to air emissions of 2.684 g cumene (emissions of oxygen are not taken into account in accordance with the methodology of this study here).

Emissions to water

The remaining part of the unreacted cumene is assumed to leave the production process with the waste water, leading to a pollution of the waste water with 64.426 g cumene. Further it was assumed that all the waste water is treated in an internal waste water plant. The removal efficiency for cumene was assumed with 90% leading to emissions of 6.443 g cumene per kg product in the treated water. The carbon contained in the removed cumene was accounted as CO₂ emissions to air (191.35 g CO₂ per kg product). The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of cumene in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 60.2.

Solid wastes

Solid wastes occurring during the production of phenol were neglected in this inventory.

60.5.4 Co- or by-products

According to the reaction scheme, besides phenol, acetone is produced in the Hock process. The stoichiometric calculation leads per kg of phenol produced to an amount of 616.3 g of acetone. In this study here, acetone is considered as a by-product and therefore not further examined.

Tab. 60.2 Energy demand, Resource demand and emissions for the production of phenol.

[per kg phenol]			Remark
INPUTS			
cumene	kg	1.342	stoechiometric calc., 95% yield
oxygen	kg	3.58E-01	stoechiometric calc., 95% yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m3	2.40E-02	estimation
Water, process, unspecified	m3	1.20E-02	estimation
transport by train	tkm	1.02E+00	calculated with standard distances
transport by lorry	tkm	1.70E-01	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
cumene, to air	kg	2.68E-03	estimated as 0.2% of input
carbon dioxide, fossil, to air	kg	1.91E-01	from waste water treatment
cumene, to water	kg	6.44E-03	calculated from mass balance
COD, BOD	kg	1.98E-02	calculated from water emissions
TOC, DOC	kg	5.79E-03	calculated from water emissions

60.6 Data quality considerations

The following table shows the data quality indicators for the inventory of phenol production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the phenol production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 60.9.

Tab. 60.3 Input / Output and uncertainty for the process “phenol, at plant (RER)”

Explanation	Name	Location	Unit	phenol, at plant	RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment	
								Location	InfrastructureProcess
								Unit	
Resource Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	Water, unspecified natural origin		m3	1.20E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	cumene, at plant	RER	kg	1.34E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	oxygen, liquid, at plant	RER	kg	3.58E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation		
	transport, freight, rail	RER	tkm	1.02E+00	1	2.09	(4,5,na,na,na,na); standard distances		
	transport, lorry 32t	RER	tkm	1.70E-01	1	2.09	(4,5,na,na,na,na); standard distances		
Output Air emission Water emission	phenol, at plant	RER	kg	1					
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input		
	Carbon dioxide, fossil		kg	1.91E-01	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Cumene		kg	2.68E-03	1	2.32	(5,5,na,na,na,5); estimation		
	BOD5, Biological Oxygen Demand		kg	1.98E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	COD, Chemical Oxygen Demand		kg	1.98E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	DOC, Dissolved Organic Carbon		kg	5.79E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	TOC, Total Organic Carbon		kg	5.79E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		
	Cumene		kg	6.44E-03	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.		

60.7 Cumulative results and interpretation

Results of the cumulative inventory of both datasets can be downloaded from the database.

60.8 Conclusions

The inventory for phenol is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if phenol is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

60.9 EcoSpold Meta Information

ReferenceFunction	Name	phenol, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Phenol, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid phenol Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	108-95-2
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production by the Hock process - there cumene is transformed into phenol by a two-stage process with (i) an oxidation of the cumene, and (ii) a cleavage to phenol and acetone. The overall process yield is of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

60.10 References

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61 Phenolic resin

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Review: Heiko Kunst, TU Berlin

61.1 Introduction

Phenolic resin are according to Hesse (2000) polycondensation products of phenols and aldehydes, in particular phenol and formaldehyde. Within the phenolic resins, two different types can be distinguished:

- *Novolacs*. Polycondensation not stopped but brought to completion. Characteristic functional group here is just the alkylidene bridge – there are no other functional groups.
- *Resols*. Synthesized by base-catalyzed polycondensation, stopped before completion. Characteristic functional groups therefore are the hydroxymethyl group and the dimethylene ether bridge.

Concerning their physical properties, phenolic resin are according to Hesse (2000) yellow to brown in color, and the coloration can very intense. All those phenolic resins that are not cross-linked, are as solids or solutions available. Concerning their miscibility or solubility with different solvents, as a function of their structure, is ranging from water soluble to that in naphtha. Cross-linked phenolic resins are all hard substances that cannot be melted. For this study, it is assumed that only non cross-linked phenolic resins are concerned. The functional unit is therefore 1 kg of pure phenolic resin.

61.2 Reserves and Resources of material

The production of phenolic resin is made out of phenols – phenol as the most important one, but also cresol, para-alkylphenol or resorcinol – and of aldehydes, the most important being formaldehyde. Therefore, all further discussion of resources equals to the discussion about the reserves of phenol and formaldehyde (see chapter 60 and chapter 40, each of this report here).

61.3 Use of material / product

According to Hesse (2000), depending on the type of phenolic resin (and if they are cross-linked or not), a huge variety of different applications are possible. One of the first was the use as varnishes (usually unlinked novolacs). Nowadays a lot of further application not only from the construction sector have been identified – e.g. in the area of printing technology, in the production of epoxy resins, as adhesives in a variety of cases, etc. etc.

In 1988, the US production was in the order of 1.38 Mt – the European production being in the same year in the order of 230 kt (Hesse (2000)).

61.4 Systems characterization

In the production process for phenolic resin the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of phenolic resin is not considered to be high. For this inventory the functional unit is 1 kg of solid phenolic resin. As process location Europe (RER) is used.

According to Hesse (2000), the whole production process of phenolic resin can be split up into several different steps. All of these steps can be carried out separately from the others, using different catalysts. A typical production plant for phenolic resin looks like:

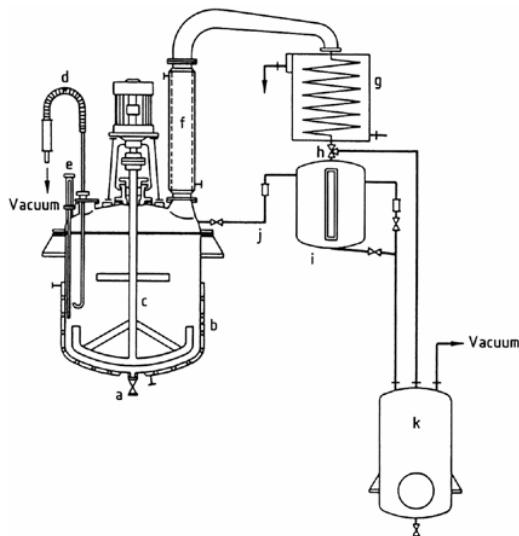


Fig. 61.1 Process chain for the production of phenolic resin (Fig.1 out of Hesse (2000) – showing outlet tap [a], heating [b], stirrer [c], evacuation system [d], thermometer [e], reflux condenser [f], main condenser [g], three-way tap [h], reflux and separation vessel [i], reflux return with siphon [j] and receiver [k])

According to their big variety, the whole process can be done at very different temperatures – starting in the area of 20°C up to 280°C. As reaction environment water, but also organic solvents or melts are in use – again in function of the type of phenolic resin produced. Often the different steps can be performed batchwise. Thereby as well the substitution reaction as well as the condensation reaction of phenol and formaldehyde are very strongly exothermic – proceeded very fast and vigorously. For this study here, a temperature of 100°C and water as reaction environment are assumed.

61.5 Phenolic resin, at plant (Location: RER)

61.5.1 Process

This dataset includes a rough estimation of the production process for phenolic resin. Due to missing production data this inventory bases on stoichiometric calculations, assuming a phenolic resin out of phenol and formaldehyde – the two most important representants of the two different categories needed for the synthesis of phenolic resins. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The overall equation for the production of phenolic resin out of phenol and formaldehyde is the following one:



61.5.2 Resources

Energy

According to Hesse (2000), the reaction is exothermic and therefore, no energy input is needed for the reaction itself. However, the different separation and condensation steps that follow the reaction need electrical energy – and therefore, data from an large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)) are used. The values for

the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) represent a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory here only the amount of 1.2 MJ kg^{-1} electricity is used.

Raw materials and Chemicals

According to the above shown reaction equation - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of phenolic resin:

- phenol, C_6H_5 : 930.693 g (9.901 mol)
- formaldehyde, CH_2O : 148.515 g (4.951 mol)

For the production a yield of 98% for the overall reaction is assumed here. Therefore 949.687 g phenol and 151.546 g formaldehyde are considered as raw materials in this inventory. A summary of the values used is given in Tab. 61.1.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the phenolic resin production.

Concerning the process water, due to a lack of specific data, for this study here, an amount of 25% of the cooling water amount is assumed – leading to an input of 6 kg water per kg phenolic resin.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg phenolic resin was included.

61.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg phenolic resin is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of phenolic resin. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input.

This assumption leads to air emissions of 1.899g phenol and 0.303 g formaldehyde.

Emissions to water

The remaining amount of unreacted phenol and formaldehyde was assumed to leave the production process with the waste water, leading to a pollution of the waste water with 17.094 g phenol and 2.728 g formaldehyde. Further it was assumed that all the waste water is treated in a internal waste water plant. The removal efficiency for both substances was assumed with 90% leading to emissions of 1.709 g phenol rsp. 0.273 g formaldehyde per kg product in the treated water. The carbon contained in the removed substances was accounted as CO₂ emissions to air (46.810 g CO₂ per kg product). The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of phenol and formaldehyde in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 61.1.

Solid wastes

Solid wastes occurring during the production of phenolic resin were neglected in this inventory.

Tab. 61.1 Energy demand, Resource demand and emissions for the production of phenolic resin.

[per kg phenolic resin]			Remark
INPUTS			
phenol	kg	0.950	stoichiometric calc., 98% yield
formaldehyde	kg	1.52E-01	stoichiometric calc., 98% yield
Electricity, medium voltage	kWh	0.333	estimation
Water, cooling, unspecified	m ³	2.40E-02	estimation
Water, process, unspecified	m ³	1.20E-02	estimation
transport by train	tkm	6.61E-01	calculated with standard distances
transport by lorry	tkm	1.10E-01	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
phenol, to air	kg	1.90E-03	estimated as 0.2% of input
formaldehyde, to air	kg	3.03E-04	estimated as 0.2% of input
carbon dioxide, fossil, to air	kg	4.68E-02	from waste water treatment
phenol, to water	kg	1.71E-03	calculated from mass balance
formaldehyde, to water	kg	2.73E-04	calculated from mass balance
COD, BOD	kg	4.18E-03	calculated from water emissions
TOC, DOC	kg	1.42E-03	calculated from water emissions

61.6 Data quality considerations

The following table shows the data quality indicators for the inventory of phenolic resin production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the phenolic resin production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller un-

certainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoicheometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 61.9.

Tab. 61.2 Input / Output and uncertainty for the process “phenolic resin, at plant (RER)”

Explanation	Name	Location	Unit	phenolic resin, at plant		uncertainty type	standardDeviation95%	GeneralComment			
				RER 0 kg							
				Location	InfrastructureProcess						
Resources Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant				
	Water, unspecified natural origin		m3	1.20E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant				
	phenol, at plant	RER	kg	9.50E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%				
	formaldehyde, production mix, at plant	RER	kg	1.52E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%				
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant				
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation				
	transport, freight, rail	RER	tkm	6.61E-01	1	2.09	(4,5,na,na,na,na); standard distances				
	transport, lorry 32t	RER	tkm	1.10E-01	1	2.09	(4,5,na,na,na,na); standard distances				
Output Air emission water emission	phenolic resin, at plant	RER	kg	1							
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input				
	Carbon dioxide, fossil		kg	4.68E-02	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Phenol		kg	1.90E-03	1	2.32	(5,na,na,na,5); estimation				
	Formaldehyde		kg	3.03E-04	1	2.32	(5,5,na,na,na,5); estimation				
	BOD5, Biological Oxygen Demand		kg	4.18E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.				
	COD, Chemical Oxygen Demand		kg	4.18E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.				
	DOC, Dissolved Organic Carbon		kg	1.42E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.				
	TOC, Total Organic Carbon		kg	1.42E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Phenol		kg	1.71E-03	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.				
	Formaldehyde		kg	2.73E-04	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.				

61.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

61.8 Conclusions

The inventory for phenolic resin is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if phenolic resin is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

61.9 EcoSpold Meta Information

ReferenceFunction	401	Name	phenolic resin, at plant
Geography	662	Location	RER
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	402	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	404	Amount	1
ReferenceFunction	490	LocalName	Phenol-Harz, ab Werk
ReferenceFunction	491	Synonyms	
ReferenceFunction	492	GeneralComment	The functional unit represent 1 kg of pure phenolic resin. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	502	CASNumber	
TimePeriod	601	StartDate	2000
TimePeriod	602	EndDate	2000
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	date of published literature
Geography	663	Text	Data used has no specific geographical origin (stoechiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	692	Text	Production from phenol and formaldehyde (as examples of the respective substance classes) with a yield of 98%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	
Representativeness	725	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	726	Extrapolations	
Representativeness	727	UncertaintyAdjustments	none

61.10 References

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62 Phosphate Rock

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 (Additions: Christian Capello, ETHZ)
 Review: Roland Hischier, EMPA St. Gallen

62.1 Introduction

Phosphorus is an essential element for plant and animal nutrition. Phosphorus is consumed primarily as a principal component of nitrogen-phosphorus-potassium (NPK) fertilisers that are used to enhance the growth of food crops throughout the world. Phosphate rock minerals are the only significant global resources of phosphorus (Jasinski 2000).

For this inventory the functional unit is 1 kg of phosphorus pentoxyde (P_2O_5) in the phosphate rock. After mining, phosphate rock is beneficiated (crushed, washed, dried etc.). Depending on the mining location and the beneficiation process, the P_2O_5 concentration in the rock can vary. For this inventory a dry-rock with 33% P_2O_5 (Morocco) and a wet-rock with 29% P_2O_5 (Florida) was investigated. The most important chemical properties of phosphate rock used in this inventory are given here (valid for beneficiated rock).

Tab. 62.1 Chemical properties of beneficiated phosphate rock

Property, Element	Unit	Moroccan ore	U.S. (Florida) ore
		per kg beneficiated Rock	per kg beneficiated Rock
Phosphorus as P_2O_5	wt. %	33	29
Fluorine, F	wt. %	3.9	3.7
CaO	wt. %	51	47
Cadmium, Cd	ppm	20	8
Lead, Pb	ppm	10	14
Arsene, As	ppm	8	8
Chromium, Cr	ppm	275	70
Copper, Cu	ppm	41	12
Manganese, Mn	ppm	21	211
Nickel, Ni	ppm	37	26
Zinc, Zn	ppm	248	77
Uranium as U_3O_8	ppm	127	166

Molecular weight of P_2O_5 : 141.94 g mol⁻¹; P: 30.97 g mol⁻¹ Bulk density of rock: ca. 1100-1400 kg m⁻³.

Composition from data (weighted average) of 9 Moroccan and 7 Florida mines (Becker 1989)

62.2 Reserves and resources of material

Phosphate rock resources occur principally as sedimentary marine phosphorites. The largest deposits are found in Northern Africa, China, the Middle East, and the United States. Significant igneous occurrences are found in Brazil, Canada, Russia, and South Africa. The phosphate minerals in both types of ore are of the apatite group. Fluorapatite $[Ca_{10}(PO_4)_6(F,OH)_2]$ predominates in igneous phosphate rocks and francolite $[Ca_{10}(PO_4)_{6-x}(CO_3)_x(F,OH)_{2+x}]$ predominates in sedimentary phosphate rocks. (EFMA, 1995). Marine phosphate accounts for approximately 85% of world commercial production.

The U.S. is the largest producer of phosphate rock (see Tab. 62.2). U.S. producers also accounted for nearly 40% of world trade in converted phosphate products (Demetriou 2001). More than 90% of the U.S. phosphate rock ore produced was used to manufacture wet-process phosphoric acid and super-phosphoric acid, which were used as intermediates in the manufacture of granular and liquid ammonium phosphate fertilizers and animal feed supplements. More than 50% of the wet-process phosphoric acid produced in the U.S. was exported in the form of upgraded granular diammonium and mono-ammonium phosphate fertilizer (MAP, DAP), triple superphosphate fertilizer (TSP), and merchant grade phosphoric acid (Jasinski 2000). Approximately 65% of the U.S. phosphate rock processing capacity is located in Florida (Maene 1999). For this inventory only the production of Moroccan and U.S. (Florida) phosphate rock was investigated.

Tab. 62.2 Phosphate rock world production (marketable rock). Only countries with more than 5 Mt a⁻¹ (gross weight) phosphate rock produced shown (Jasinski 2000).

Countries	Production, gross weight				Production as P ₂ O ₅			
	1999		2000		1999		2000	
	Mt a ⁻¹	%	Mt a ⁻¹	%	Mt a ⁻¹	%	Mt a ⁻¹	%
China	20.0 r)	15	19.4 e)	15	6.00 r)	14	5.82 e)	14
Jordan	6.0 r)	4	5.5 f)	4	1.99 r)	5	1.82 f)	4
Morocco *)	22.8 r)	17	21.6 f)	16	7.50 r)	17	7.20 f)	17
Russia	11.4 r)	8	11.1 e)	8	4.40 r)	10	4.30 e)	10
Tunisia	8.0 r)	6	8.3 f)	6	2.40 e)	6	2.50	6
United States	40.6	30	38.6 f)	29	11.80	27	11.20 f)	27
Other countries	28.2	21	28.5	21	9.12	21	9.26	22
Total	137.0 r)	100	133.0	100	43.20 r)	100	42.10	100

Table includes data available at May 8, 2001. Data for major phosphate rock-producing countries derived in part from the International Fertiliser Industry Association; other figures are from official country sources where available.

r) Revised; e) Estimated; f) Reported figure; *) Includes production from Western Sahara.

62.3 Use of material / product

Mineral fertilizers account for approximately 80% of phosphate use in the world, shared by detergents (12%), animal feeds (5%) and speciality applications (3%), e.g. food additives, metal treatment etc. (Maene 1999). World production of phosphate rock has decreased from 137 Mt in 1999 to 133 Mt in 2000 (see Tab. 62.2). The United States, Morocco, China, and Russia accounted for 65% of total production, by order of output (Jasinski 2000). In addition to lower production, world-wide shipments of phosphate rock decreased for both export and internal consumption, while stocks increased (Demetriou 2001). The closure of two phosphoric acid plants in the Netherlands and the opening of a phosphate rock mine in Canada reduced trade of phosphate rock in Europe and North America (Jasinski 2000). Of a total world phosphate fertiliser consumption in 1997/98, China accounted for 27%, North America for 15%, West and Central Europe for 13%, and India for 12%. It should be noted that the former Soviet Union consumed only 2% of the world's phosphate fertilisers in 1997 (Maene 1999).

62.4 Systems characterization

Because of the different ore contents, beneficiation procedure (dry/ wet) and the different way of phosphogypsum disposal during phosphoric acid production, two locations for phosphate rock production were investigated (Morocco, Florida). The process chain was assessed as shown in the following figure. There were two processes modelled:

- Phosphate rock, beneficiated, wet, 29% P₂O₅ in crude ore, at plant (location: US)
- Phosphate rock, beneficiated, dry, 33% P₂O₅ in crude ore, at plant (location: MA)

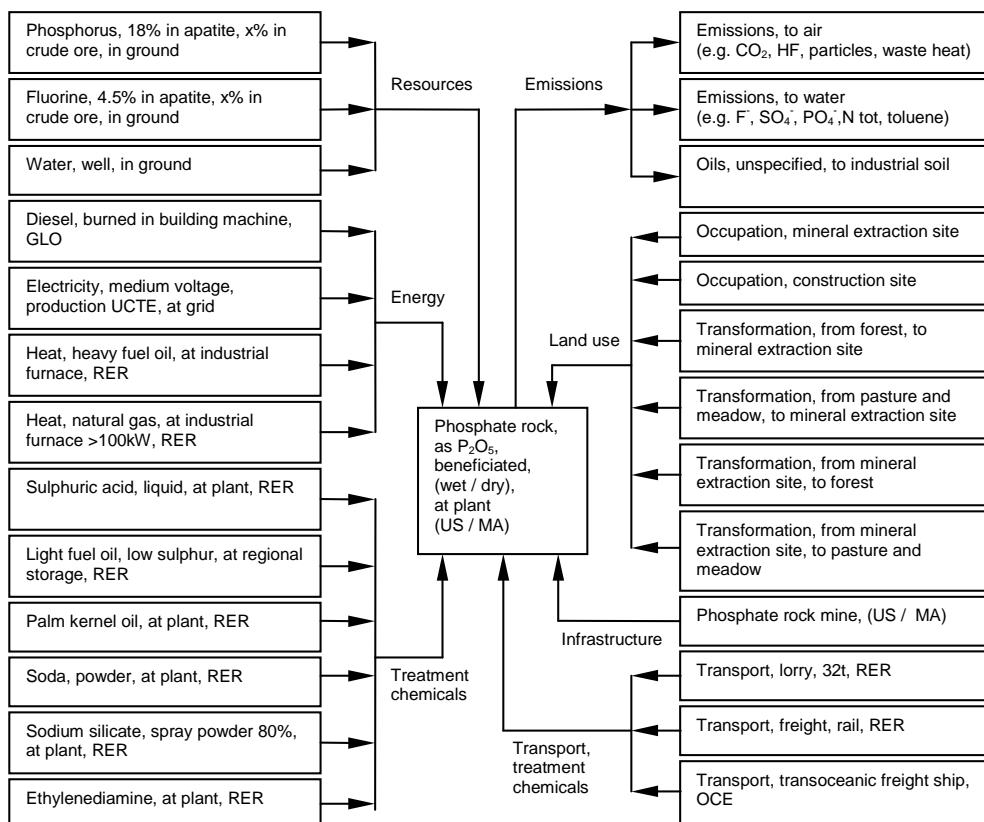


Fig. 62.1 Process chain for the production of phosphate rock

The two investigated phosphate rock mining processes represent a share of 40-50% of the world production of phosphate rock. The main resource used is phosphorous in ground, but also fluorine was considered because of the production of fluosilic acid during the production of phosphoric acid. Other possible outputs such as uranium or magnesium oxide were neglected. Especially for beneficiation of U.S. phosphate rock large amounts of water (from wells) are used to separate the phosphate ore from clay and pebbles. In addition to the electrical energy and fuel for mining and beneficiation processes, fuel oil and natural gas are used for drying the beneficiated rock or, to a smaller extend, for calcination steps within beneficiation. Drying and calcination is seldom used within the U.S. phosphate rock production. The most important auxiliary materials for beneficiation were considered in this inventory. As output there is only phosphate rock to account. Most emissions to the air are already included in the preceding process of the furnace, fuel use, or electricity chain. Additional emissions to the air, water and ground were considered, e.g. primary dust and fluorine. The overburden and the matrix ore, which is recycled to the mine, were not considered as waste.

62.5 Phosphate Rock, at plant (location: Florida, Morocco)

62.5.1 Process

The steps needed for phosphate rock production are different depending on ore, P_2O_5 concentration, organic matter content, and on the used process for phosphoric acid production. For this inventory characteristic process chains for U.S. (Florida) and Moroccan ores were investigated. These two ores were selected because of the differences in their production paths and the importance of their market share on world production (see Tab. 62.2). The Moroccan ores are mainly open mined but also underground mining is used (for around 14% of the production). In the U.S. only open mining is used.

A simplified process scheme of phosphate rock production in Morocco is shown in Fig. 62.2 and for production in Florida in Fig. 62.3.

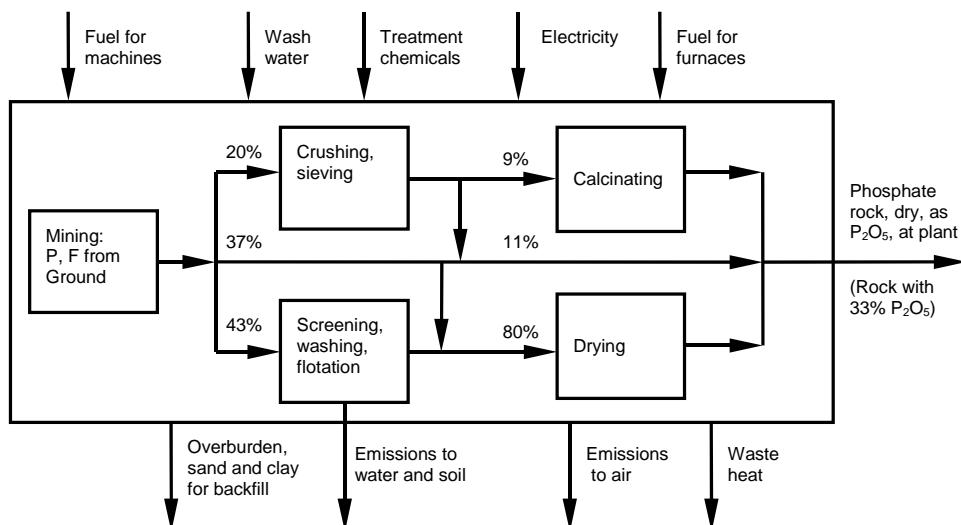


Fig. 62.2 Simplified process of phosphate rock production in Morocco

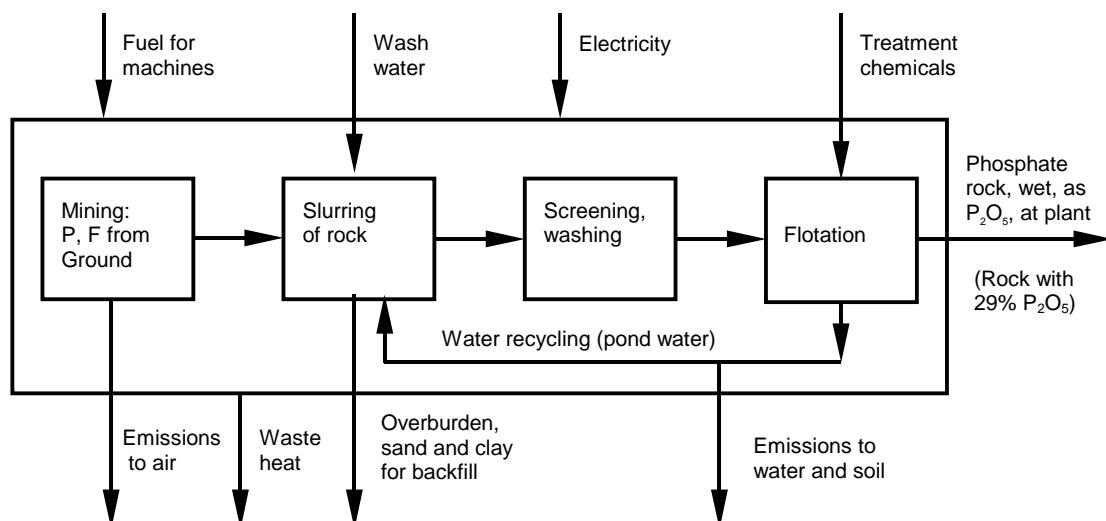


Fig. 62.3 Simplified process of phosphate rock production in Florida

Most phosphate ores have to be concentrated or beneficiated before they can be used or sold on the international phosphate market (EFMA 1995). Commercial phosphate rock has a P₂O₅ concentration of usually 30 to 33%. As Tab. 62.3 shows, especially the phosphate rock production in Florida leads to large amounts of waste rock due to the low P₂O₅ concentration of the ore. Moroccan phosphate rock has a higher P₂O₅ concentration (around 30%) and therefore nearly no waste rock is produced in the beneficiation step.

The wet beneficiated phosphate rock may be dried or calcined, depending on its organic content. Florida rock is relatively free of organics and is for the most part no longer dried or calcined. Unlike Florida rock, phosphate rock mined from other reserves can contain organics and must be heated to 760 to 870 °C to remove them (EPA 1993a). For this inventory no calcination or drying was assumed for Florida phosphate rock. Some of Moroccan phosphate rock is calcinated due to a concentration of organics of 8 – 10% (Landbank 1994). Of the phosphate rock produced in Morocco, 43% are beneficiated by washing and drying, 9% are calcinated, 11% are dry processed (sieving, crushing), and 37% are only dried (El Hourai et al. 1998).

Tab. 62.3 Phosphate Rock Production of the United States (Jasinski & Lindsay 2001)

Production step	Florida and North Carolina				Idaho and Utah			
	as Rock		as P ₂ O ₅		as Rock		as P ₂ O ₅	
	Mt a ⁻¹	%	Mt a ⁻¹	%	Mt a ⁻¹	%	Mt a ⁻¹	%
Mine production, crude ore (100%)	149.25	100	13.97	100	9.19	100	1.93	100
Marketable production (beneficiated)	33.00	22	9.67	69	5.82	64	1.64	85
Loss	116.25	78	4.30	31	3.37	36	0.29	15

Table includes averaged data for crop year 2000 and 2001 (July 1999 to June 2001).

P₂O₅ content before beneficiation: 9% (Florida and North Carolina), 21% (Idaho and Utah).

P₂O₅ content after beneficiation for both locations around 29%

62.5.2 Resources

Phosphorus, 18% in apatite, x% in crude ore, in ground

As resource from nature the crude phosphate ore is the most important. Currently, most phosphate rock production worldwide is extracted using opencast dragline or open-pit shovel/excavator mining methods. This method is employed widely in parts of the U.S., Morocco, and Russia (UNEP 2001). According to data from Becker 1989, 14% of the phosphate rock produced in Morocco is mined underground. In Florida all phosphate rock produced is mined open.

For the Moroccan phosphate rock mined underground, 1.3 kg of crude ore from ground is needed per kg of beneficiated rock (Landbank 1994). Oversize and waste rock occurs during calcination (0.13 g per kg of beneficiated rock) and extraction (50 g per kg of beneficiated rock). Also some loss in weight occurs during calcination (water vapour, oxidation of organics).

For open mining, the topsoil and overburden have to be removed before mining the ore bed. For the open mining in the Benguerir mine in Morocco, an average strip ratio (total kg moved rock per kg ore) of 3.5:1 was reported (Mining Technology 2002). According to Becker 1989, the strip ratio may rise in unfavourable cases up to 8:1. For the open mining in Morocco a strip ratio of 5:1 was assumed. Thus, for every 1 kg of crude ore extracted 5 kg of material have to be moved and 4 kg of overburden and topsoil are piled. Like for the underground mining there are only small losses during beneficiation. There were no specific data available so the same amount of crude ore was assumed (1.3 kg per kg of beneficiated rock). With data from Mining Technology 2002 and Becker 1989 it was estimated that

the Moroccan crude ore contains in average 27% P₂O₅. Therefore, the Moroccan crude phosphate ore is accounted as “phosphorus, 18% in apatite, 12% in crude ore, in ground”. 0.156 kg phosphorus is needed for 1 kg of beneficiated rock (33% P₂O₅), which equals a P recovery efficiency of 92%.

For the phosphate rock mined in Florida, 4.5 kg of crude ore from ground (with 9% P₂O₅) is needed for 1 kg of beneficiated rock (Jasinski & Lindsay 2001). For every 4.5 kg of crude ore extracted 11 kg of material have to be moved and 6.5 kg of overburden and topsoil are piled (EPA 1994). The U.S. crude phosphate ore is accounted as “phosphorus, 18% in apatite, 4% in crude ore, in ground”. 0.18 kg phosphorus is needed for 1 kg of beneficiated rock (29% P₂O₅), which equals a P recovery efficiency of 70%. This value is in accordance with the value of 60-70% presented in Becker 1989.

Fluorine, 4.5% in apatite, x% in crude ore, in ground

Fluorine as a resource from nature was considered because in some plants a part of the fluorine is recovered as fluosilicic acid during phosphoric acid production. According to data from Becker 1989 for 16 mines in Morocco and the U.S., phosphate rock contains about 0.037 kg fluorine per kg beneficiated rock. With this data the amount of fluorine extracted from the ground was estimated, assuming 5% loss during beneficiation for the Moroccan rock and 18% loss for the U.S. phosphate rock.

For the Moroccan phosphate rock the fluorine in the crude phosphate ore is accounted as “Fluorine, 4.5% in apatite, 3% in crude ore, in ground”, so 0.039 kg fluorine is needed for 1 kg of beneficiated rock (33% P₂O₅). For the U.S. phosphate rock, the fluorine in the crude phosphate ore is accounted as “Fluorine, 4.5% in apatite, 1% in crude ore, in ground”, so 0.045 kg fluorine is needed for 1 kg of beneficiated rock (29% P₂O₅).

Other resources from ground

The overburden, topsoil, and waste rock were neglected in this inventory as resources because they are backfilled into the mine and used for reclamation. Also the amounts of magnesium (ca. 0.5 wt. % in rock) and uranium (ca. 0.015 wt. % in rock) in the phosphate rock were not considered as resource. In most cases they are not recovered due to economical reasons. Therefore, most of the 8 U.S. recovery plants for uranium from phosphate rock were shut down. In some cases it is necessary to remove magnesium due to higher concentrations of the element in the rock, which is unwanted in the product. These cases were neglected in this inventory.

Process energy, mining

There was no detailed information on the energy consumption of the different mining operations available. According to Kippenberger 1999, the mining operation requires in average 0.4 MJ final energy per kg P₂O₅ or 0.8 MJ of primary energy (60% of world production surveyed, crude ore with 15.6% P₂O₅, 3 kg moved material per kg crude ore). Of the final energy, around 2/3 is electrical energy. In Patyk & Reinhardt 1997 the mining operations are assumed to take place only with diesel driven engines consuming 0.2 MJ diesel per 1.28 kg of crude ore containing 25% P₂O₅. According to Zhang 2001, in Florida mines 0.054 MJ electricity per kg beneficiated rock is needed to slurry and transport the rock to the beneficiation plant. For the underground mining in Morocco, an electricity demand of 0.042 MJ per 1.25 kg of calcinated phosphate rock or 0.15 MJ per kg P₂O₅ was reported (Landbank 1994).

For this inventory all open mining operations (in Morocco and Florida) were calculated with the data from Kippenberger 1999, based on the mass of moved material. For open mining in Florida a demand of 0.38 MJ electricity and 0.19 MJ diesel per kg P₂O₅ were assumed (crude ore with 9% P₂O₅, 2.4 kg moved material per kg crude ore). For the open mining in Morocco, a demand of 0.25 MJ electricity and 0.12 MJ diesel per kg P₂O₅ were assumed (crude ore with 28% P₂O₅, 5 kg moved material per kg crude ore). For the underground mining in Morocco (14% of production) the data of Landbank 1994

was used. For the average mining in Morocco a final energy demand of 0.24 MJ electricity and 0.10 MJ diesel per kg P₂O₅ were calculated.

Due to the continuous mining and reclaiming process in phosphate mines, it was assumed that the applied values include the energy used for back filling of waste rock and earth moving during the reclamation process.

Process energy, beneficiation

The process of crushing, sieving and calcination consumes 0.34 MJ heat and 0.119 MJ electricity per kg of beneficiated (33% P₂O₅) phosphate rock (Landbank 1994).

For screening, washing and flotation of the phosphate rock a consumption of 0.18 MJ electricity per kg of beneficiated phosphate rock (32% P₂O₅) was assumed (Patyk & Reinhardt 1997). For drying washed rock, 0.43 MJ heat per kg of beneficiated phosphate rock (32% P₂O₅) are needed (Patyk & Reinhardt 1997). Kippenberger 1999 reports an average of 0.9 MJ final energy per kg P₂O₅ processed (1.5 MJ of primary energy, around 45% electricity). These data is in good accordance with the other sources but it was not used because it does not show the specific process steps.

For this inventory the values were based on the mass of beneficiated rock. The following values were used for each process step per kg of beneficiated rock:

- Crushing, sieving and calcination: 0.34 MJ heat, 0.119 MJ electricity
- Crushing, sieving only: 0.119 MJ electricity
- Screening, washing and flotation: 0.18 MJ electricity
- Drying: 0.43 MJ heat

For the phosphate rock mined in Florida, a washing and flotation process was included, but no drying or calcination. Therefore, the beneficiation steps account with 0.18 MJ electricity per kg beneficiated phosphate rock. According to data from U.S. Census Bureau 1997, in average 0.075 MJ fossil fuels and 0.23 MJ electricity were used per kg beneficiated phosphate rock for the whole mining process in the U.S. phosphate industry. The data applied in this inventory for the Florida rock show higher electricity consumption (0.29 MJ kg⁻¹) and lower fuel use (0.06 MJ kg⁻¹) due to the different mining process in Florida (more material moved with draglines and conveyors, no drying of rock). In order to assess data for wet rock production as it is used in Florida the differences to the average U.S. data for the energy consumption were not considered. Of the Moroccan phosphate rock 43% are beneficiated by washing and drying, 9% are calcinated and 11% are dry processed (sieving, crushing) and 37% are only dried (El Hourai et al. 1998). For the average mining in Morocco a final energy demand of 0.10 MJ electricity and 0.37 MJ heat per kg P₂O₅ was calculated, according to the share of the different production processes.

Water resources

For the phosphate rock mining, washing and flotation in Florida, large amounts of water are used. Industry-wide about 95.6% of the water needed in the mining process is reused. In average the consumption of pumped well-water was 0.0029 m³ per kg of beneficiated phosphate rock (averaged data from 1991 to 2000 of 7 companies (Florida Phosphate Council 2001)). The rainwater which is also incorporated in the water cycle (around 0.0027 m³ per kg of beneficiated phosphate rock according to the data presented in (EPA 1994)) was not considered as resource in this inventory.

For the open mining and beneficiation of phosphate rock in Morocco, water is used for washing in some mines. There was no data available about the amount of water used. Due to the dry climate in Morocco, most of the used water for washing needs to be taken from groundwater reservoirs. The of

water demand will be smaller due to the smaller amount of overburden in the Moroccan phosphate ore. Because of the lack of data, the same amount (0.0029 m^3 per kg of beneficiated phosphate rock) as in the inventory for the U.S. phosphate rock was used for mines with washing operations. For the underground mining and beneficiation of phosphate rock in Morocco, no use of water was reported (Landbank 1994). For the average Moroccan phosphate rock, a water demand of 0.00125 m^3 per kg of beneficiated phosphate rock was assumed because only 43% of the produced rock is washed.

Treatment chemicals

For washing and flotation, sulphuric acid, fuel oil, fatty acid, soda ash, sodium silicate and amines are used. The flotation process and values for sulphuric acid consumption (8-15 kt 96% H_2SO_4 per year) of a large phosphate producer (5.5 Mt a^{-1} of beneficiated rock) in Florida are presented in EPA 1994. For this inventory the average values per kg of beneficiated phosphate rock presented in Patel & Schreiber 2001 were used for the Florida phosphate rock. For the Moroccan phosphate rock no data was available for the detailed washing and flotation process. Therefore, the same amounts of chemicals were applied as for the Florida phosphate rock. Because only 43% of the Moroccan phosphate rock is washed in average, only 43% of the values of the treatment chemicals was applied. As approximation for the fatty acid consumption palm kernel oil was used. The amine consumption was approximated with ethylenediamine.

Used processes

For all electricity demands the process “electricity, medium voltage, production UCTE, at grid” was assumed. To produce the heat for drying and calcination, natural gas and fuel oil is used (EPA 1993a). It was assumed that 50% of the heat is produced with natural gas. For heat production the processes “heat, natural gas, at industrial furnace $>100\text{kW}$, RER” and “heat, heavy fuel oil, at industrial furnace, RER” were used. For diesel fuel used for mining operations, the process “diesel, burned in building machine, GLO” was used.

Tab. 62.4 Phosphate rock production. Resource demands for Moroccan and U.S. (Florida) ore

Resource, Use	Unit	Moroccan ore		U.S. (Florida) ore	
		per kg Rock a)	per kg P ₂ O ₅	per kg Rock b)	per kg P ₂ O ₅
Phosphorus, in ground as crude ore, in ground	kg	0.156	0.47	0.18	0.62
	kg	1.3	3.9	4.5	15.5
Fluorine, in ground	kg	0.039	0.118	0.045	0.155
Water, well, in ground	m ³	0.00125	0.0038	0.0029	0.01
Fuel, for mining operations ¹	MJ	0.034	0.103	0.055	0.19
Electricity, for mining operations	kWh	0.020	0.066	0.031	0.106
Heat, for beneficiation ²	MJ	0.375	1.135	no drying	no drying
Electricity, for beneficiation	kWh	0.028	0.084	0.050	0.172
Light fuel oil, for flotation	kg	0.0013	0.0039	0.003	0.0103
palm kernel oil, for flotation	kg	0.0009	0.0026	0.002	0.0069
Soda, powder, for flotation	kg	0.0009	0.0026	0.002	0.0069
Sodium silicate, spray powder 80%, for flotation	kg	0.00026	0.0008	0.0006	0.0021
Ethylenediamine, at plant	kg	0.00034	0.0010	0.0008	0.0028
Sulphuric acid, liquid, for flotation	kg	0.0013	0.0039	0.003	0.0103

Value per kg P₂O₅ refers to the beneficiated phosphate rock with: a) 33% P₂O₅ content ; b) 29% P₂O₅ content.

Processes used for assessing the energy demand: All electricity as, medium voltage, production UCTE, at grid

¹ Diesel, burned in building machine.

² 50% heat, heavy fuel oil, at industrial furnace; 50% heat, natural gas, at industrial furnace >100kW

62.5.3 Emissions

Emissions to air

The CO₂ emissions from the calcination process of the phosphate rock are caused from the oxidised organic content of the rock and from the burning of fuel in the calcinator. The CO₂ emissions of the carbon content is given in (Landbank 1994) with 0.073 kg CO₂ per kg of calcinated rock. This value is obviously based on a stocheometric calculation. Calcination is only applied to a part of the total production, the average emission factors for the Moroccan phosphate rock presented in Tab. 45.3 were calculated for a production share of 11% (8.03 g CO₂ kg⁻¹). For the U.S. phosphate rock no calcination was assumed and therefore also no such emissions.

Further CO₂-, CO-, SO₂, NO_x and other emissions caused by the burning of the fuel in the furnace are included in the linked process. Data concerning particle and fluoride emissions were calculated with the emission factors presented in EPA 1993a. Scrubbers are commonly used for phosphate rock drying and calcination, therefore the controlled emission factors (with scrubber) presented in EPA 1993a were applied.

Due to the fact that particle emissions of the fuel-burning are included in the used furnace process, 8.7 mg TPM MJ⁻¹ heat were subtracted from the (controlled) emission factor presented in EPA 1993a; Table 11.21-3, to prevent double counting. The subtracted value was estimated from emission factors (50% fuel oil with 17.3 mg TPM MJ⁻¹, 50% natural gas with 0.1 mg TPM MJ⁻¹) as presented in Lükewille et al. 2001. This leads to additional particle emissions of 31 mg TPM per kg beneficiated phosphate rock for drying (dryer with scrubber emitting 35 mg TPM kg⁻¹, 0.43 MJ kg⁻¹ heat needed) and 97 mg TPM per kg beneficiated phosphate rock for calcination (calciner with scrubber emitting

100 mg TPM kg⁻¹, 0.34 MJ kg⁻¹ heat needed). The particle size distribution for controlled particle emissions of the drying and calcination step was assessed according to EPA 1986; page B1-69, B1-73. For drying, the shares used were 3% for > 10 µm, 8% for 2.5-10 µm and 89% for < 2.5 µm particle size. For calcination the shares used were 2% for > 10 µm, 4% for 2.5-10 µm and 94% for < 2.5 µm particle size.

The fluorine emissions within the calcination- and drying-process were assessed with the controlled emission factors given in EPA 1993a; Table 11.21-6. For a dryer with scrubber, 4.8 mg fluorine per kg beneficiated phosphate rock and for a calciner with scrubber, 0.81 mg fluoride per kg beneficiated phosphate rock were assumed.

Due to the fact that drying and calcination is only applied to a part of the total production, the average emission factors for the Moroccan phosphate rock presented in Tab. 45.3 were calculated for a production share of 9% being calcinated and 80% being dried. For the U.S. phosphate rock no calcination or drying was assumed and therefore also no such emissions. No fluorine emissions were accounted for crushing and sieving operations. All fluorine emissions were counted as hydrogen fluoride.

Emissions from material handling systems are difficult to quantify because several different systems are used to convey rock. The emission factor for transfer and storage given in EPA 1993a is referenced to unpublished test data from 1970. The emission factor states emissions of 2 g TPM per kg beneficiated rock. Because of the lack of documentation and the age of the test data, data quality and representativeness of this emission factor is low (EPA 1993b). Estimations were made with help of the emission factors presented in NPi 2001 for coal mines and metalliferous mines. The estimated emission factors ranged between 0.4-1.5 g TPM per kg beneficiated rock. Due to lack of better data an average emission factor of 1 g TPM per kg beneficiated rock was used for this inventory. The particle size distribution for particle emissions from material handling was estimated with data for rock screening and handling and unpaved road transport as presented in CEIDARS 2000; ID 371, ID 415. It was assumed that the particle emissions occur mainly during the transport of the rock and the particle distribution is therefore comparable to road transport in stone crushing, sand and gravel industry as presented in EPA 1998; Table 4-21. The particle size distribution for PM 2.5 ranges from 7% to 17% and for PM 10 from 25% to 59%. For this inventory the following distribution was used for the particle emissions from material transfer and storage: 58% for > 10 µm, 30% for 2.5-10 µm and 12% for < 2.5 µm particle size.

While in Florida the phosphate rock is grinded mainly wet without releasing significant emissions to air, in Morocco a part of the rock (11%) is crushed and sieved dry. The particle emissions from this operation was assessed with the controlled emission factors for grinding given in EPA 1993a; Table 11.21-3. For a grinder with fabric filter, particle emissions of 2.2 mg TPM per kg beneficiated phosphate rock were assumed. The particle size distribution for controlled particle emissions of the grinding operation was assessed according to EPA 1986; Page B1-77. The shares used were 10% for > 10 µm, 65% for 2.5-10 µm and 25% for < 2.5 µm particle size. Dry crushing is only applied to a part of the total production in Morocco. Therefore, the average emission factors for the Moroccan phosphate rock presented in Tab. 45.3 were calculated assuming a production share of 11%. For the U.S. phosphate rock no dry crushing was assumed and therefore also no such emissions.

Tab. 62.5 Phosphate rock production. Emissions to air for Moroccan and U.S. (Florida) ore

Emission, process	Unit	Moroccan ore	U.S. (Florida) ore		
		per kg Rock a)	per kg P ₂ O ₅	per kg Rock b)	per kg P ₂ O ₅
CO ₂ , from calcination ¹	kg	8.03 * 10 ⁻³	24.3 * 10 ⁻³	no calcination	no calcination
Fluorine, from calcination ²	kg	0.073 * 10 ⁻⁶	0.22 * 10 ⁻⁶	no calcination	no calcination
Fluorine, from drying ²	kg	3.84 * 10 ⁻⁶	11.6 * 10 ⁻⁶	no drying	no drying
Particle (TPM), from calcina- tion ³	kg	8.73 * 10 ⁻⁶	26.5 * 10 ⁻⁶	no calcination	no calcination
Particle (TPM), from drying ³	kg	25 * 10 ⁻⁶	75.8 * 10 ⁻⁶	no drying	no drying
Particle (TPM), from crushing ⁴	kg	0.24 * 10 ⁻⁶	0.73 * 10 ⁻⁶	no crushing	no crushing
Particles, from Transfer and storage ⁵	kg	1.0 * 10 ⁻³	3.0 * 10 ⁻³	1.0 * 10 ⁻³	3.4 * 10 ⁻³
Emission of ²³⁸ U, in dust ⁷	kBq	1.55 * 10 ⁻³	4.70 * 10 ⁻³	1.70 * 10 ⁻³	5.86 * 10 ⁻³
Emission of ²³⁴ U, in dust ⁷	kBq	1.55 * 10 ⁻³	4.70 * 10 ⁻³	1.70 * 10 ⁻³	5.86 * 10 ⁻³
Emission of ²³⁰ Th, in dust ⁷	kBq	1.55 * 10 ⁻³	4.70 * 10 ⁻³	1.70 * 10 ⁻³	5.86 * 10 ⁻³
Emission of ²²⁶ Ra, in dust ⁷	kBq	1.65 * 10 ⁻³	5.01 * 10 ⁻³	1.70 * 10 ⁻³	5.86 * 10 ⁻³
Emission of ²¹⁰ Pb, in dust ⁷	kBq	0.93 * 10 ⁻³	2.82 * 10 ⁻³	0.68 * 10 ⁻³	2.34 * 10 ⁻³
Emission of ²¹⁰ Po, in dust ⁷	kBq	0.93 * 10 ⁻³	2.82 * 10 ⁻³	0.68 * 10 ⁻³	2.34 * 10 ⁻³
Emission of ²³² Th, in dust ⁷	kBq	0.017 * 10 ⁻³	0.050 * 10 ⁻³	0.030 * 10 ⁻³	0.103 * 10 ⁻³
Waste heat, to air	MJ	0.17	0.54	0.29	1.00
Particle distribution ⁸					
Particle (TPM), total	kg	1.03 * 10 ⁻³	3.13 * 10 ⁻³	1.00 * 10 ⁻³	3.45 * 10 ⁻³
Particle, > 10 µm, total	kg	0.58 * 10 ⁻³	1.76 * 10 ⁻³	0.58 * 10 ⁻³	2.00 * 10 ⁻³
Particle, 2.5-10 µm, total	kg	0.30 * 10 ⁻³	0.92 * 10 ⁻³	0.30 * 10 ⁻³	1.03 * 10 ⁻³
Particle, < 2.5 µm, total	kg	0.15 * 10 ⁻³	0.46 * 10 ⁻³	0.12 * 10 ⁻³	0.41 * 10 ⁻³

Value per kg P₂O₅ refers to the beneficiated phosphate rock with: a) 33% P₂O₅ content ; b) 29% P₂O₅ content.

Calcination applied to 9% of Moroccan phosphate rock. Drying applied to 43% of Moroccan phosphate rock.

¹ CO₂ emissions from burned organics (Landbank 1994), CO₂ emission of the furnace process has to be added.

² Calciner and dryer with scrubber (EPA 1993a, Table 11.21-6), counted as hydrogen fluoride.

³ Calciner and dryer with scrubber (EPA 1993a, Table 11.21-3), particle emission of the furnace process excluded.

⁴ Grinder with fabric filter (EPA 1993a, Table 11.21-3), applied for 11% of Moroccan rock and 0% for Florida rock.

⁵ Estimated as 50% of uncontrolled emissions presented in (EPA 1993a, Table 11.21-3). Poor data quality.

⁷ Calculated of specific radionuclide activity and particle emission.

⁸ Calculated from particle distribution of the different emission sources.

There were few data available on radioactive emissions to air. Calculated with the uncontrolled emission factor for a grinder as presented in EPA 1993a; Table 11.21-6, the emission rate is equal to the specific activity of the rock itself. For the controlled emission the value given was about 4 times smaller than the specific activity of the rock. Because most dust emissions occur during the mining operation itself and less in the beneficiation steps, the radioactive emissions to air were calculated as the specific activity of the rock multiplied with the total particle emissions (TPM). This simplified approach leads to large uncertainties, but was assumed to give a reasonable estimate of the real emissions. Also the specific activity of the rock varies largely. According to EPA 1993a, the specific activity ranges from 217 Bq kg⁻¹ to 9880 Bq kg⁻¹ for different U.S. phosphate rocks. For this inventory the data for ²³⁸U, ²²⁶Ra and ²³²Th presented in Azouazi et al. 2001 for Florida and Moroccan phosphate rocks were used as average values for the radionuclide activity. These activity values are for the Moroccan phosphate rock 1700 Bq kg⁻¹ ²³⁸U, 1700 Bq kg⁻¹ ²²⁶Ra and 30 Bq kg⁻¹ ²³²Th. For the Florida

phosphate rock the activity values of 1500 Bq kg^{-1} ^{238}U , 16 Bq kg^{-1} ^{232}Th and 1600 Bq kg^{-1} ^{226}Ra were used. To calculate the emissions of the ^{238}U decay products ^{234}U and ^{230}Th equilibrium, conditions as measured in Azouazi et al. 2001 and Poole et al. 1995 were assumed. Therefore, the same activity as for ^{238}U was used for the calculation. For ^{210}Pb and ^{210}Po , only 80% of the ^{238}U activity for the Florida ore and 60% of the ^{238}U activity for the Moroccan ore was used according to data of Azouazi et al. 2001 and Poole et al. 1995. Further decay products and other radionuclides were neglected.

To calculate the waste heat to the air, it was assumed that 100% of the waste heat from electricity use is emitted to air. The waste heat of the fuel use is already included in the fuel processes (diesel in building machine, fuel in furnace) and therefore not considered here.

Emissions to Water

For the underground phosphate rock mining and beneficiation in Morocco, water emissions were neglected due to the dry processing route according to Landbank 1994. For the open phosphate rock mining (with washing and drying) in Morocco, no specific data were available about water emissions. For those cases, as approximation, the emission values for the U.S. (Florida) mines were applied.

The amount of waste water for the U.S. phosphate rock production was derived from the water balance of one plant in Florida¹⁸, described in EPA 1994. In this plant the controlled runoff of 0.0017 m^3 per kg of beneficiated phosphate rock is discharged to a river. There is no further treatment of these effluents, which are characterised by monitoring data of the outfall (from year 1991) presented in EPA 1994, Table 5. In addition to the accounted share of water, around 0.028 m^3 rainwater per kg of beneficiated phosphate rock fall on the production area (see water balance in EPA 1994). It was assumed that 40% of this water runs uncontrolled into the river or leaches and the rest evaporates. This run-off water was assumed to have the same pollution as the controlled effluent. With these assumptions a total wastewater effluent of 0.013 m^3 per kg of beneficiated phosphate rock has to be accounted as emissions to water (river).

The emission values for BOD, COD, DOC and TOC were calculated from the emission data. It was assumed that the values of COD and BOD are equal. For the TOC value the share of volatile suspended solids was considered (but not in the DOC value). The phosphorus emission was estimated to be 2/3 of the 30-day average limit value of 3 g P m^{-3} given by the Florida Department of Environmental Protection (DEP 1996).

In Morocco only 43% of the phosphate rock is washed. There was no information available on the specific water emissions for phosphate rock production in Morocco. Therefore, 43% of the values for the emissions to water of the U.S. phosphate rock were applied. A summary of the values is given in the following table.

¹⁸ Annual production of 5.5 Mt a^{-1} of beneficiated phosphate rock (accounting for around 14 % of U.S. production)

Tab. 62.6 Phosphate rock production. Emissions to water for Moroccan and U.S. (Florida) ore

Emission	Unit	Moroccan ore		U.S. (Florida) ore	
		per kg Rock a)	per kg P ₂ O ₅	per kg Rock b)	per kg P ₂ O ₅
Fluoride ¹	kg	5.59E-06	1.69E-05	1.30E-05	4.48E-05
Sulphate ²	kg	3.69E-04	1.12E-03	8.59E-04	2.96E-03
Toluene ³	kg	6.71E-08	2.03E-07	1.56E-07	5.38E-07
Nitrogen (Kjeldahl) ⁴	kg	4.37E-06	1.32E-05	1.02E-05	3.50E-05
Phosphor ⁵	kg	1.12E-05	3.39E-05	2.60E-05	8.97E-05
Suspended solids (TSS) ⁶	kg	2.80E-05	8.47E-05	6.50E-05	2.24E-04
BOD ⁷	kg	8.33E-05	2.52E-04	1.94E-04	6.68E-04
COD ⁷	kg	8.33E-05	2.52E-04	1.94E-04	6.68E-04
DOC ⁷	kg	6.15E-08	1.86E-07	1.43E-07	4.93E-07
TOC ⁷	kg	2.24E-05	6.78E-05	5.20E-05	1.79E-04
Radioactive species, alpha emitters ⁸	kBq	5.40E-04	1.64E-03	1.26E-03	4.33E-03

Value per kg P₂O₅ refers to the beneficiated phosphate rock with: a) 33% P₂O₅ content ; b) 29% P₂O₅ content.

No values for total ammonia and phosphates available. pH value of wastewater: 6.42 - 7.7

¹ For beneficiated phosphate rock with 29% P₂O₅ content and 0.002 m³ of wastewater per kg of phosphate rock.

¹ Limit values for fluoride emission according to EPA 1994; Table 5: 0 - 2.7 g m⁻³. Assumed average: 1 g m⁻³.

² Geometric average of limit values for sulphate emission (17.8 – 245.4 g m⁻³) according to EPA 1994; Table 5.

³ Value of toluene according to EPA 1994; Page 39. Value: 0.012 g m⁻³

⁴ Geometric average of limit values for Kjeldahl nitrogen (0.21 - 2.91 g m⁻³) according to EPA 1994; Table 5.

⁵ Emission value estimated as 2 g m⁻³, equals 2/3 of 30-day average limit value of U.S. emission regulations.

⁶ Most likely value of (total) TSS (5 g m⁻³) according to EPA 1994; Table 5. Extreme values: 0 - 28 g m⁻³

⁷ Calculated emission values. COD = BOD assumed, TOC includes volatile share of suspended solids.

⁸ Geometric average of limit values for gross alpha emitters (37 - 252 Bq m⁻³) according to EPA 1994; Table 5.

62.5.4 Emissions to soil and wastes

Two main waste products are generated during the beneficiation and processing of phosphate rock: sand tailings and phosphatic clays (from washing and flotation). Tailings are commonly used to backfill mine cuts. In the production plants in Florida the phosphatic clays are pumped as 3 to 5% solids slurry to large, diked areas where the clay solids slowly settle and the supernatant water is reused in the mining operations. Clay represents 25% of the crude ore. The phosphorus remaining in the disposed sand and clay (up to 30% of the mined phosphorus), which is filled back into the mine pit was not accounted as emission to the soil.

There were no data of emissions to the soil available in tailings- and clay-pond areas for the Florida phosphate mines. The treatment chemicals used for flotation undergo a biological degradation during the process of use and recycling and settling, but some will remain to some extend in the soil. The used fuel oil shows the lowest biodegradation (10% in 20 days for fuel oil alone and 45% in 20 days for a fatty acid fuel oil mixture, aerobic conditions) and may therefore pollute the soil in the clay pond area. According to Patel & Schreiber 2001, 90 to 95% of the fuel oil used will end up in the clay and sand. For this inventory it was assumed that 50% of the used fuel oil would be emitted as soil emission. Other emissions to the soil of the treatment chemicals were neglected.

For the Moroccan ore only little solid waste is generated due to the high grade of the crude ore. From these waste tailings no emissions were accounted. The same assumptions for the fate of the treatment chemicals were made for the Moroccan mine as for the Florida phosphate mine.

Other wastes and materials generated at the site include waste oil, dragline grease, spent solvents, laboratory wastes, tires, batteries, trash, sanitary wastewater, and sewage sludge (EPA 1994). These wastes undergo the usual waste treatment or recycling and were neglected in this inventory due to their small amount.

Tab. 62.7 Phosphate rock production. Emissions to soil for Moroccan and U.S. (Florida) ore

Emission	Unit	Moroccan ore		U.S. (Florida) ore	
		per kg Rock a)	per kg P₂O₅	per kg Rock b)	per kg P₂O₅
Oils, unspecified, industrial ¹	kg	0.64 * 10 ⁻³	1.93 * 10 ⁻³	1.49 * 10 ⁻³	5.10 * 10 ⁻³

Value per kg P₂O₅ refers to the beneficiated phosphate rock with: a) 33% P₂O₅ content ; b) 29% P₂O₅ content.

¹ 90% of fuel oil Input as emission in sand and clay, biological degradation 45% assumed.

62.5.5 Land use

From a typical Florida phosphate mine 2500 kg of phosphate rock per m² of land are extractable. In 1995 0.76 m² were mined per metric ton of phosphate rock (Zhang 2001). In this value also the land used beside the mine pit is included (e.g. pond area). Averaged data of the mined area between 1970-1989 indicate a land use of 0.64 m² per metric tons of beneficiated phosphate rock in Florida (Long & Orne 1990). According to data from Pressacco 2001, Craig & Pflaum 2001, and EPA 1994, the land use varies largely for the individual mines and ranges from 0.2 to 1.6 m² per metric tons of beneficiated phosphate rock. Tailings from the beneficiation step are commonly used to backfill mine cuts: the overburden stockpiled nearby is spread over the tailings to produce a stable land form with a variety of potential uses. The waste clay settling ponds occupy from 20 to 40% of the land area mined (average value is 33% according to Long & Orne 1990), so that a significant portion of mined land will not be available for load-supporting construction uses. These clay ponds require 5 to 15 years, depending on dewatering techniques, to crust over enough (15-20% solids level) to support cattle (Long & Orne 1990). The land use of the settling ponds has to be added to the land use of the mining. A rough classification of world-wide phosphate mining areas according to vegetation zones was used to estimate the land transformations (Kippenberger 1999). The area needed for the beneficiation plant is considered within the infrastructure process.

For the inventory of the Florida phosphate mine, a transformation to mineral extraction site of 0.64 * 10⁻³ m² per kg beneficiated phosphate rock (29% P₂O₅ content) was assumed. According to Long & Orne 1990, about 30% of the mined area was previously woodland. The rest (mainly pasture and rangeland) was accounted as pasture. After reclamation of the mining area, the share of the woodland sank to 15% and the area with pasture increased. During mining operation, an occupation as "mineral extraction site" of the whole site with an average operating time of 20 years (13-35 years) was assumed (Pressacco 2001, Craig & Pflaum 2001). The reclamation is included in the 20 years operating time due to continuous reclamation of mined land sectors. This leads to an occupation of 12.8 * 10⁻³ m² a per kg phosphate rock. For the settling pond area, further 15 years of occupation must be accounted for reclamation after mine closure because this area is continuously occupied during the mine operation. With a clay pond area of 1/3 of the total mining site this leads to an occupation of 3.2 * 10⁻³ m² a per kg phosphate rock. This occupation was considered as "construction site".

There were no specific data available for the land use of Moroccan phosphate mines. For the open mining in Morocco (86% of the production) it was assumed that only 40% of the land is transformed and occupied per kg of beneficiated phosphate rock in comparison to the Florida mines (this is equal to a transformation of 0.26 * 10⁻³ m² kg⁻¹). This assumption can be justified by the smaller amount of waste rock and clay, which leads to much smaller pond areas and stacks. Also, only 43% of the rock is washed in the plant and dry processing is more often used. Therefore, the land use is limited to the mining pit, the waste rock piles and in some cases to a smaller pond area. For the underground mining

in Morocco (14% of the production), there are even smaller amounts of overburden and nearly no stacked topsoil. Also, these mines do not apply washing and therefore a pond area is not needed. For this mining type, the land transformation and occupation was assumed to be 50% of the value for open pit mining in Morocco.

For the inventory of the average Moroccan phosphate mine, a transformation to mineral extraction site of $0.24 * 10^{-3} \text{ m}^2$ per kg beneficiated phosphate rock (33% P_2O_5 content) was calculated. The use of the mining area after reclamation was assumed to be the same as before. Further, it was assumed that 100% of the area was pasture or savannah. During mining operation, an occupation as “mineral extraction site” with an operating time of 20 years was assumed like for the Florida mine. Further 15 years of occupation were accounted for the reclamation of the settling pond areas occupying 10% of the average mining area. This results in a total occupation of $5.2 * 10^{-3} \text{ m}^2$ per kg phosphate rock with 33% P_2O_5 content (thereof, $0.4 * 10^{-3} \text{ m}^2$ are accounted as “construction site” for pond reclamation).

Tab. 62.8 Phosphate rock production. Land use for Moroccan and U.S. (Florida) ore

Land use	Unit	Moroccan ore		U.S. (Florida) ore	
		per kg Rock a)	per kg P_2O_5	per kg Rock b)	per kg P_2O_5
Occupation as mineral extraction site ¹	m^2 a	$4.8 * 10^{-3}$	$14.4 * 10^{-3}$	$12.8 * 10^{-3}$	$44.1 * 10^{-3}$
Occupation as construction site ²	m^2 a	$0.4 * 10^{-3}$	$1.1 * 10^{-3}$	$3.2 * 10^{-3}$	$10.9 * 10^{-3}$
Transformation from forest ²	m^2	-	-	$0.19 * 10^{-3}$	$0.66 * 10^{-3}$
Transformation from pasture and meadow	m^2	$0.24 * 10^{-3}$	$0.72 * 10^{-3}$	$0.45 * 10^{-3}$	$1.54 * 10^{-3}$
Transformation to mineral extraction site	m^2	$0.24 * 10^{-3}$	$0.72 * 10^{-3}$	$0.64 * 10^{-3}$	$2.21 * 10^{-3}$
Transformation from mineral extraction site	m^2	$0.24 * 10^{-3}$	$0.72 * 10^{-3}$	$0.64 * 10^{-3}$	$2.21 * 10^{-3}$
Transformation to forest ³	m^2	-	-	$0.10 * 10^{-3}$	$0.33 * 10^{-3}$
Transformation to pasture and meadow	m^2	$0.24 * 10^{-3}$	$0.72 * 10^{-3}$	$0.54 * 10^{-3}$	$1.88 * 10^{-3}$

Value per kg P_2O_5 refers to the beneficiated phosphate rock with: a) 33% P_2O_5 content ; b) 29% P_2O_5 content.

¹ Assumed operating time of the mine: 20 years. Includes reclamation of mining site due to continuous reclamation.

² Additional 15 years reclamation time for settling pond area after mine closure.

³ 30% of the area mined in Florida was forest before mining and 15% will be reclaimed to forest.

62.5.6 Transport processes and infrastructure

The transport of treatment chemicals from the producer to the mine was considered with the standard distances for base chemicals (100 km road and 600 km rail) except of the sulphuric acid. Sulphuric acid is normally produced in a plant nearby because it is also used for downstream processing of phosphoric acid. For sulphuric acid, only a transport distance of 100 km by road was assumed. For the Moroccan mine additional 1600 km sea transport and 100 km road transport (from the port to the mine) were applied.

The infrastructure of the mine, i.e. the buildings and the equipment, is discussed in Kap. 62.6. The infrastructure was assessed as plant with an output of 5 Mta-1 of beneficiated phosphate rock. With this value the infrastructure needed per kg phosphate rock was calculated.

Tab. 62.9 Phosphate rock production. Transport processes and infrastructure for Moroccan and U.S. (Florida) ore

Infrastructure & Transports	Unit	Moroccan ore		U.S. (Florida) ore	
		per kg Rock a)	per kg P ₂ O ₅	per kg Rock b)	per kg P ₂ O ₅
Phosphate rock mine ⁴	unit	$10.0 * 10^{-12}$	$30.3 * 10^{-12}$	$10.0 * 10^{-12}$	$34.5 * 10^{-12}$
Transport, lorry, 32t	tkm	$0.87 * 10^{-3}$	$2.57 * 10^{-3}$	$1.14 * 10^{-3}$	$3.93 * 10^{-3}$
Transport, freight, rail	tkm	$2.22 * 10^{-3}$	$6.54 * 10^{-3}$	$5.04 * 10^{-3}$	$17.4 * 10^{-3}$
Transport, transoceanic freight ship ²	tkm	$5.92 * 10^{-3}$	$17.4 * 10^{-3}$	-	-

Value per kg P₂O₅ refers to the beneficiated phosphate rock with: a) 33% P₂O₅ content ; b) 29% P₂O₅ content.

¹Assumed operating time of the mine: 20 years. Plant with 5 Mt a⁻¹ rock production.

²It was assumed that the treatment chemicals for the Moroccan mine are imported from Europe by sea.

62.6 Phosphate rock mine, infrastructure (Morocco, Florida),

There were no detailed studies available on the infrastructure used in phosphate mines. The values for infrastructure were estimated from some figures from two phosphate mines in Florida and one in Morocco. In the mines in Florida phosphate rock is mostly mined with draglines, slurried and then transported to the beneficiation plant in pipes. The overburden is often moved with conveyors to the stacks. Some data to the equipment used is given in Mining Technology 2001 and EPA 1994. In Morocco the open mined phosphate rock is excavated with draglines. According to the equipment list of a mine presented in Mining Technology 2002, the rock and the overburden are transported mostly with haul trucks and less with conveyors. Due to the weak data available for the infrastructure demand, many assumptions were made. The following data was calculated for a mine with an annual production of 5 Mt beneficiated phosphate rock. A summary of the estimated values is given in Tab. 62.10.

The weight and type of the equipment used for the mining operation was roughly estimated with data from an equipment manufacturer (Bucyrus-Erie 2002). The amount and type of material used for the storage tanks for flotation chemicals, fuel, and product storage was estimated with data from Pressacco 2001 and EPA 1994. The metal used for pipes and tanks was assumed to be recycled (as stated in EPA 1994) and therefore no burden for disposal of these parts was considered. The estimated values for the materials used as production equipment has to be regarded as rough estimate and does not show an average of the industry. The building infrastructure was estimated with help of pictures from various production sites. The value applied to the process “building, hall” is therefore only very rough estimates.

The infrastructure of fuel driven equipment is already considered in the processes “diesel, burned in building machine” and “heat, at industrial furnace”. Therefore, only the electrical driven equipment has to be considered here. It was assumed that the draglines, conveyors, slurry pumps, and the equipment for grinding and washing were electrical driven. Excavators, haulers, bulldozers, and equipment for drying were not considered here due to the assumed operation with fuel. For the estimated total weight of the draglines (3-4 draglines a 1000 t) the process “hydraulic digger” (15 t per unit) and for the other mining equipment (about 340 t) the process “building machine” was applied. For the belt conveyor, the process “conveyor belt, at plant, RER” was used which represents a conveyor with 0.5 m belt width. The weight of the conveyor, which was calculated for a conveyor with 3 m belt width, was transformed to the length of the 0.5 m belt conveyor using a factor of 15 kg m⁻¹. For the slurry pipes (0.56 m diameter) a weight of 140 t km⁻¹ (steel) and a pipe length of 2.8 km (Morocco) and 6.5 km Florida was applied. The equipment used for crushing, washing, and flotation was approximated with the module “industrial machine, heavy, unspecified, at plant”. Equipment transport from producer to the mine was considered for the draglines, the conveyor, the slurry pipe as well as for the equipment assessed as “building machine” and “industrial machine, heavy”.

Tab. 62.10 Infrastructure for 5 Mt a⁻¹ production plant of Moroccan and U.S. (Florida) phosphate rock.

Resource, Use	Unit	Moroccan ore production	U.S. (Florida) ore production
		per unit (plant)	per kg Rock
		kg	kg
Dragline approximated as hydraulic digger ¹	kg unit	3.98 * 10 ⁶ 265	39.8 * 10 ⁻⁶ 2.7 * 10 ⁻⁹
Conveyor belt, at plant ²	kg m	0.81 * 10 ⁶ 54 * 10 ³	8.1 * 10 ⁻⁶ 0.54 * 10 ⁻⁶
Slurry pipe as steel, low-alloyed, at plant	kg	0.39 * 10 ⁶	3.9 * 10 ⁻⁶
Drawing of pipes, steel	kg	0.39 * 10 ⁶	3.9 * 10 ⁻⁶
Other equipment as Industrial machine, heavy, unspecified, at plant ³	kg	0.34 * 10 ⁶	3.4 * 10 ⁻⁶
liquid storage tank, chemicals, organics ⁴	kg unit	0.42 * 10 ⁶ 1.01	4.2 * 10 ⁻⁶ 10.1 * 10 ⁻¹²
Transport, lorry, 32t ⁵	tkm	1.10 * 10 ⁶	11.0 * 10 ⁻⁶
Transport, freight, rail ⁵	tkm	2.21 * 10 ⁶	22.1 * 10 ⁻⁶
Transport, transoceanic freight ship ⁵	tkm	8.83 * 10 ⁶	88.3 * 10 ⁻⁶
Building hall for washing, flotation	m3	387 * 10 ³	3.9 * 10 ⁻⁶
Building hall for crushing, drying	m3	88 * 10 ³	0.9 * 10 ⁻⁶
Building hall for other purpose	m3	11 * 10 ³	0.1 * 10 ⁻⁶
Total amount for: building, hall, steel construction ⁶	m2	69 * 10 ³	0.7 * 10 ⁻⁶
Occupation as construction site ⁷	m ² a	0.2 * 10 ⁶	2.0 * 10 ⁻⁶
Occupation as industrial area ⁸	m ² a	0.8 * 10 ⁶	8.0 * 10 ⁻⁶
Transformations ⁹	m ²	40 * 10 ³	0.4 * 10 ⁻⁶
			100 * 10 ³
			1.0 * 10 ⁻⁶

Value per kg P₂O₅ refers to the beneficiated phosphate rock with: a) 33% P₂O₅ content ; b) 29% P₂O₅ content.

¹ Value in units was calculated with a machine weight of 15 t as used in the process "hydraulic digger".

² Value in meter was calculated with a conveyor weight of 15 kg m⁻¹ for a 0.5 m wide belt conveyor.

³ Approximation for crushing, washing and flotation equipment.

⁴ Storage tanks for flotation chemicals, fuel and approximation for product bins. Tank weight 416 t per unit.

⁵ Equipment transport from producer to the mine: 200 km road, 400 km rail and 1600 km sea for Morocco; 100 km road and 200 km rail for Florida.

⁶ Total for flotation-, drying- and other-buildings in m² calculated from volume with the standard height for of 7 m.

⁷ Time needed for building and removal of the plant after closure: 5 years

⁸ Assumed operating time of the plant: 20 years.

⁹ Includes exchanges for transformation from pasture and meadow to industrial area.

The area needed for the infrastructure of the beneficiation plant is small (less than 0.5% of the total area) and was estimated to be about 20'000 m² per Mt annual production of beneficiated phosphate rock for a phosphate rock plant with washing and flotation (out of data from Pressacco 2001). For this land use a transformation to industrial area was assumed. During the average 20 years of mining operation an occupation as industrial area was assumed. For the construction and the removal of the buildings additional 5 years were assumed for occupation as construction site. These values for land transformation and occupation for the production buildings were applied for the Florida mine. The

phosphate rock production plant in Morocco will occupy a smaller area, because often no flotation plant is needed. For the Moroccan plant 40% of the land occupation of the Florida plant was assumed.

62.7 Data quality considerations

Tab. 62.11 shows the data quality indicators for the inventory of wet phosphate rock production in Florida and Tab. 62.12 the dry rock production in Morocco. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation, and sample size. The highest uncertainties exist for the particle emissions during transfer and storage. Also emissions to water have a high uncertainty because of the lack of data for uncontrolled run off. In general, the data presented for the Moroccan phosphate production are more uncertain, because few Moroccan product data was available and therefore often data of U.S. producers was used to assess the Moroccan mining processes. There are also high uncertainties concerning the amount of infrastructure applied to the modules. This value seems less important due to the high throughput of the mines. In general the infrastructure data (presented in Tab. 62.13 and Tab. 62.14) has a high uncertainty because only few data was available for the assessment.

Tab. 62.11 In- / outputs for the module “phosphate rock, as P2O5, beneficiated, wet, at plant”, location US

Process output: 1 kg, phosphate rock, as P2O5, beneficiated, wet, at plant, US		Uncertainty			Comment
Name, Location	Value	Unit	Type	Score	
From technosphere	diesel, burned in building machine, GLO	1.90E-1 MJ	lognorm	2,3,3,2,3,3	1.26
	electricity, medium voltage, production UCTE, at grid, UCTE	2.78E-1 kWh	lognorm	2,3,3,5,4,3	1.55
	light fuel oil, at regional storage, RER	1.03E-2 kg	lognorm	2,3,3,5,4,3	1.55
	palm kernel oil, at plant, RER	6.90E-3 kg	lognorm	2,3,3,5,5,3	2.04
	soda, powder, at plant, RER	6.90E-3 kg	lognorm	2,3,3,5,4,3	1.55
	sodium silicate, spray powder 80%, at plant, RER	2.10E-3 kg	lognorm	2,3,3,5,4,3	1.55
	ethylenediamine, at plant, RER	2.80E-3 kg	lognorm	2,3,3,5,5,3	2.04
	sulphuric acid, liquid, at plant, RER	1.03E-2 kg	lognorm	2,3,3,5,4,3	1.55
	phosphate rock mine, US	3.45E-11 unit	lognorm	4,5,1,5,4,5	3.38
	transport, lorry 32t, RER	3.93E-3 tkm	lognorm	4,5,1,5,4,5	2.38
Resources	transport, freight, rail, RER	1.74E-2 tkm	lognorm	4,5,1,5,4,5	2.38
	Phosphorus, 18% in apatite, 4% in crude ore, in ground	6.20E-1 kg	lognorm	1,2,1,3,1,1	1.06
	Fluorine, 4.5% in apatite, 1% in crude ore, in ground	1.55E-1 kg	lognorm	3,3,4,3,1,1	1.24
	Water, well, in ground	1.00E-2 m3	lognorm	1,3,1,3,1,1	1.07
	Occupation, mineral extraction site	4.41E-2 m2a	lognorm	2,3,5,3,1,1	1.78
	Occupation, construction site	1.09E-2 m2a	lognorm	4,3,5,3,3,1	1.88
	Transformation, from forest	6.60E-4 m2	lognorm	2,3,5,3,1,1	2.24
	Transformation, from pasture and meadow	1.54E-3 m2	lognorm	2,3,5,3,1,1	2.24
	Transformation, to mineral extraction site	2.21E-3 m2	lognorm	2,3,5,3,1,1	2.24
	Transformation, from mineral extraction site	2.21E-3 m2	lognorm	2,3,5,3,1,1	2.24
Emissions	Transformation, to forest	3.30E-4 m2	lognorm	2,3,5,3,1,1	2.24
	Transformation, to pasture and meadow	1.88E-3 m2	lognorm	2,3,5,3,1,1	2.24
	Particulates, > 10 µm, to air, low population density	2.00E-1 kg	lognorm	3,5,5,3,3,5	1.94
	Particulates, > 2.5 µm, and < 10µm, to air, low pop. dens.	1.03E-3 kg	lognorm	3,5,5,3,3,5	2.38
	Particulates, < 2.5 µm, to air, low population density	4.10E-4 kg	lognorm	3,5,5,3,3,5	3.38
	Uranium-238, to air, low population density	5.86E-3 kBq	lognorm	4,5,5,3,3,5	3.41
	Uranium-234, to air, low population density	5.86E-3 kBq	lognorm	4,5,5,3,3,5	3.41
	Thorium-230, to air, low population density	5.86E-3 kBq	lognorm	4,5,5,3,3,5	3.41
	Radium-226, to air, low population density	5.86E-3 kBq	lognorm	4,5,5,3,3,5	3.41
	Lead-210, to air, low population density	2.34E-3 kBq	lognorm	4,5,5,3,3,5	3.41
	Polonium-210, to air, low population density	2.34E-3 kBq	lognorm	4,5,5,3,3,5	3.41
	Thorium-232, to air, low population density	1.03E-4 kBq	lognorm	4,5,5,3,3,5	3.41
	Heat, waste, to air, low population density	1.00E+0 MJ	lognorm	2,3,3,2,3,3	1.26
	Fluoride, to water, river	4.48E-5 kg	lognorm	3,4,3,3,3,5	1.66
	Sulfate, to water, river	2.96E-3 kg	lognorm	3,4,3,3,3,5	1.66
	Toluene, to water, river	5.38E-7 kg	lognorm	3,4,3,3,3,5	3.13
	Nitrogen, to water, river	3.50E-6 kg	lognorm	3,4,3,3,3,5	1.66
	Phosphorus, to water, river	8.97E-5 kg	lognorm	3,4,3,3,3,5	1.66
	Suspended solids, unspecified, to water, river	2.24E-4 kg	lognorm	3,4,3,3,3,5	1.66
	BOD5, Biological Oxygen Demand, to water, river	6.68E-4 kg	lognorm	4,5,3,3,3,5	1.74
	COD, Chemical Oxygen Demand, to water, river	6.68E-4 kg	lognorm	4,5,3,3,3,5	1.74
	DOC, Dissolved Organic Carbon, to water, river	4.93E-7 kg	lognorm	4,5,3,3,3,5	1.74
	TOC, Total Organic Carbon, to water, river	1.79E-4 kg	lognorm	4,5,3,3,3,5	1.74
	Radioactive species, alpha emitters, to water, river	4.33E-3 kBq	lognorm	3,4,3,3,3,5	3.13
	Oils, unspecified, to soil, industrial	5.10E-3 kg	lognorm	5,5,3,3,4,5	2.13

Tab. 62.12 In- / outputs for the module “phosphate rock, as P2O5, beneficiated, dry, at plant”, location MA

Process output: 1 kg, phosphate rock, as P2O5, beneficiated, dry, at plant, MA							
Name, Location		Value	Unit	Uncertainty		Comment	
				Type	Score	St.Dev.	
From technosphere	diesel, burned in building machine, GLO	1.03E-1	MJ	lognorm	2,3,3,2,3,3	1.26	61% of world production 1994
	heat, heavy fuel oil, at industrial furnace 1MW, RER	5.68E-1	MJ	lognorm	2,3,3,5,4,3	1.55	Technology-mix estimated, Location RER
	heat, natural gas, at industrial furnace >100kW, RER	5.68E-1	MJ	lognorm	2,3,3,5,4,3	1.55	Technology-mix estimated, Location RER
	electricity, medium voltage, production UCTE, at grid, UCTE	1.50E-1	kWh	lognorm	2,3,3,5,4,3	1.55	61% of world production 1994, European mix
	light fuel oil, at regional storage, RER	3.90E-3	kg	lognorm	3,3,3,5,4,3	1.56	Average data from U.S study, Location RER
	palm kernel oil, at plant, RER	2.60E-3	kg	lognorm	3,3,3,5,5,3	2.05	Average data from U.S study; proxy used
	soda, powder, at plant, RER	2.60E-3	kg	lognorm	3,3,3,5,4,3	1.56	Average data from U.S study, Location RER
	sodium silicate, spray powder 80%, at plant, RER	8.00E-4	kg	lognorm	3,3,3,5,4,3	1.56	Average data from U.S study, Location RER
	ethylenediamine, at plant, RER	1.00E-3	kg	lognorm	3,3,3,5,5,3	2.05	Average data from U.S study; proxy used
	sulphuric acid, liquid, at plant, RER	3.90E-3	kg	lognorm	3,3,3,5,4,3	1.56	Average data from U.S study, Location RER
	phosphate rock mine, MA	3.03E-11	unit	lognorm	4,5,1,5,4,5	3.38	Estimated with weak data from 2 sites
	transport, lorry 32t, RER	2.57E-3	tkm	lognorm	4,5,1,5,4,5	2.38	Estimated with standard distances for europe
	transport, freight, rail, RER	6.54E-3	tkm	lognorm	4,5,1,5,4,5	2.38	Estimated with standard distances for europe
	transport, transoceanic freight ship, OCE	1.74E-2	tkm	lognorm	4,5,1,5,4,5	2.38	Estimated for import from Europe
Resources	Phosphorus, 18% in apatite, 12% in crude ore, in ground	4.70E-1	kg	lognorm	1,2,1,3,1,1	1.06	Data of year 1999 / 2000 from Morocco used
	Fluorine, 4.5% in apatite, 3% in crude ore, in ground	1.18E-1	kg	lognorm	3,3,4,3,1,1	1.24	Data for process loss estimated
	Water, well, in ground	3.80E-3	m3	lognorm	4,5,1,5,4,1	1.64	Estimated from data of U.S. mines
	Occupation, mineral extraction site	1.44E-2	m2a	lognorm	4,5,5,5,4,1	2.13	Estimated from data of U.S. mines
	Occupation, construction site	1.10E-3	m2a	lognorm	4,5,5,5,4,1	2.13	Estimated from data of U.S. mines
	Transformation, from pasture and meadow	7.20E-4	m2	lognorm	4,5,5,5,4,1	2.56	Estimated from data of U.S. mines
	Transformation, to mineral extraction site	7.20E-4	m2	lognorm	4,5,5,5,4,1	2.56	Estimated from data of U.S. mines
	Transformation, from mineral extraction site	7.20E-4	m2	lognorm	4,5,5,5,4,1	2.56	Estimated from data of U.S. mines
	Transformation, to pasture and meadow	7.20E-4	m2	lognorm	4,5,5,5,4,1	2.56	Estimated from data of U.S. mines
	Carbon dioxide, fossil, air, low population density	2.43E-2	kg	lognorm	2,4,2,1,1,5	1.24	Data from 1 mine in Morocco
	Hydrogen fluoride, to air, low population density	1.18E-5	kg	lognorm	2,4,5,5,3,4	2.32	U.S. data from 1973
	Particulates, > 10 µm, to air, low population density	1.76E-3	kg	lognorm	3,5,5,5,3,5	1.95	U.S. data from 1970 and data of coal mining
	Particulates, > 2.5 µm, and < 10µm, to air, low. pop. dens.	9.20E-4	kg	lognorm	3,5,5,5,3,5	2.39	U.S. data from 1970 and data of coal mining
	Particulates, < 2.5 µm, to air, low population density	4.60E-4	kg	lognorm	3,5,5,5,3,5	3.39	U.S. data from 1970 and data of coal mining
Emissions	Uranium-238, to air, low population density	4.70E-3	kBq	lognorm	4,5,5,5,3,5	3.42	Calculated from dust emissions
	Uranium-234, to air, low population density	4.70E-3	kBq	lognorm	4,5,5,5,3,5	3.42	Calculated from dust emissions
	Thorium-230, to air, low population density	4.70E-3	kBq	lognorm	4,5,5,5,3,5	3.42	Calculated from dust emissions
	Radium-226, to air, low population density	5.01E-3	kBq	lognorm	4,5,5,5,3,5	3.42	Calculated from dust emissions
	Lead-210, to air, low population density	2.82E-3	kBq	lognorm	4,5,5,5,3,5	3.42	Calculated from dust emissions
	Polonium-210, to air, low population density	2.82E-3	kBq	lognorm	4,5,5,5,3,5	3.42	Calculated from dust emissions
	Thorium-232, to air, low population density	5.00E-5	kBq	lognorm	4,5,5,5,3,5	3.42	Calculated from dust emissions
	Heat, waste, to air, low population density	5.40E-1	MJ	lognorm	2,3,3,2,3,3	1.26	Calculated from electricity demand
	Fluoride, to water, river	1.69E-5	kg	lognorm	3,4,3,5,4,5	1.88	Data from 1 U.S. mine (1990) and estimates
	Sulfate, to water, river	1.12E-3	kg	lognorm	3,4,3,5,4,5	1.88	Data from 1 U.S. mine (1990) and estimates
	Toluene, to water, river	2.03E-7	kg	lognorm	3,4,3,5,4,5	3.32	Data from 1 U.S. mine (1990) and estimates
	Nitrogen, to water, river	1.32E-5	kg	lognorm	3,4,3,5,4,5	1.88	Data from 1 U.S. mine (1990) and estimates
	Phosphorus, to water, river	3.39E-5	kg	lognorm	3,4,3,5,4,5	1.88	Data from 1 U.S. mine (1990) and estimates
	Suspended solids, unspecified, to water, river	8.47E-5	kg	lognorm	3,4,3,5,4,5	1.88	Data from 1 U.S. mine (1990) and estimates
	BOD5, Biological Oxygen Demand, to water, river	2.52E-4	kg	lognorm	4,5,3,5,4,5	1.95	Calculated from measured data
	COD, Chemical Oxygen Demand, to water, river	2.52E-4	kg	lognorm	4,5,3,5,4,5	1.95	Calculated from measured data
	DOC, Dissolved Organic Carbon, to water, river	1.86E-7	kg	lognorm	4,5,3,5,4,5	1.95	Calculated from measured data
	TOC, Total Organic Carbon, to water, river	6.78E-5	kg	lognorm	4,5,3,5,4,5	1.95	Calculated from measured data
	Radioactive species, alpha emitters, to water, river	1.64E-3	kBq	lognorm	3,4,3,5,4,5	3.32	Data from 1 U.S. mine (1990) and estimates
	Oils, unspecified, to soil, industrial	1.93E-3	kg	lognorm	5,5,3,5,5,5	2.57	Estimation from data of chemical demand

Tab. 62.13 In- / outputs for the module “phosphate rock mine”, location US

Process output: 1 unit, phosphate rock mine, US							
Name, Location		Value	Unit	Uncertainty		Comment	
				Type	Score	St.Dev.	
From technosphere	transport, lorry 32t, RER	6.50E+5	tkm	lognorm	4,5,nA,5,nA,nA	2.11	Estimated with standard distances for europe
	transport, freight, rail, RER	1.30E+6	tkm	lognorm	4,5,nA,5,nA,nA	2.11	Estimated with standard distances for europe
	hydraulic digger, RER	2.27E+2	unit	lognorm	5,5,1,3,5,5	2.33	Estimated from data of 2 U.S. mines; proxy used
	conveyor belt, at plant, RER	1.25E+5	m	lognorm	5,5,1,3,5,5	2.33	Estimated from data of 2 U.S. mines; proxy used
	Industrial machine, heavy, unspecified, at plant, RER	3.30E+5	kg	lognorm	5,5,1,3,5,5	2.33	Estimated from data of 2 U.S. mines; proxy used
	steel, low-alloyed, at plant, RER	9.10E+5	kg	lognorm	5,5,3,3,4,5	1.89	Estimated from data of 2 U.S. mines
	drawing of pipes, steel, RER	9.10E+5	kg	lognorm	5,5,3,3,4,5	1.89	Estimated from data of 2 U.S. mines
	liquid storage tank, chemicals, organics, CH	1.42E+0	unit	lognorm	5,5,3,3,5,5	2.34	Estimated from data of 2 U.S. mines; proxy used
	building, hall, steel construction, CH	1.33E+5	m2	lognorm	5,5,1,3,5,5	2.33	Estimated from photograph of 1 U.S. mine
	Occupation, industrial area	2.00E+6	m2a	lognorm	5,4,1,3,1,5	1.84	Estimated from map of 1 U.S. mine
	Occupation, construction site	5.00E+5	m2a	lognorm	5,4,1,3,1,5	1.84	Estimated from map of 1 U.S. mine
	Transformation, from pasture and meadow	1.00E+5	m2	lognorm	4,4,1,3,1,5	2.11	Estimated from map of 1 U.S. mine
	Transformation, to industrial area	1.00E+5	m2	lognorm	4,4,1,3,1,5	2.11	Estimated from map of 1 U.S. mine

Tab. 62.14 In- / outputs for the module “phosphate rock mine”, location MA

Process output: 1 unit, phosphate rock mine, MA		Value	Unit	Uncertainty			Comment
	Name, Location			Type	Score	St.Dev.	
From technosphere	transport, lorry 32t, RER	1.10E+6	tkm	lognorm	4,5,nA,5,nA,nA	2.11	Estimated with standard distances for europe
	transport, freight, rail, RER	2.21E+6	tkm	lognorm	4,5,nA,5,nA,nA	2.11	Estimated with standard distances for europe
	transport, transoceanic freight ship, OCE	8.83E+6	tkm	lognorm	4,5,nA,5,nA,nA	2.11	Estimated for import from Europe
	hydraulic digger, RER	2.65E+2	unit	lognorm	5,5,1,5,5,5	2.34	Estimated from data of 2 mines; proxy used
	conveyor belt, at plant, RER	5.40E+4	m	lognorm	5,5,1,5,5,5	2.34	Estimated from data of 2 mines; proxy used
	Industrial machine, heavy, unspecified, at plant, RER	3.40E+5	kg	lognorm	5,5,1,5,5,5	2.34	Estimated from data of 2 mines; proxy used
	steel, low-alloyed, at plant, RER	3.90E+5	kg	lognorm	5,5,3,5,4,5	1.91	Estimated from data of 2 mines
	drawing of pipes, steel, RER	3.90E+5	kg	lognorm	5,5,3,5,4,5	1.91	Estimated from data of 2 mines
	liquid storage tank, chemicals, organics, CH	1.01E+0	unit	lognorm	5,5,3,5,5,5	2.35	Estimated from data of 2 mines; proxy used
	building, hall, steel construction, CH	6.90E+4	m2	lognorm	5,5,1,5,5,5	2.34	Estimated from photograph of 2 mines
Resources	Occupation, industrial area	8.00E+5	m2a	lognorm	5,5,1,5,4,5	2.13	Estimated from map of 1 U.S. mine
	Occupation, construction site	2.00E+5	m2a	lognorm	5,5,1,5,4,5	2.13	Estimated from map of 1 U.S. mine
	Transformation, from pasture and meadow	4.00E+4	m2	lognorm	5,5,1,5,4,5	2.56	Estimated from map of 1 U.S. mine
	Transformation, to industrial area	4.00E+4	m2	lognorm	5,5,1,5,4,5	2.56	Estimated from map of 1 U.S. mine

62.8 Cumulative results and interpretation

Results of the cumulative inventory of both datasets can be downloaded from the database.

62.9 Conclusions

The production of phosphate rock has a large variety due to different ore grades (small or large oversize) beneficiation processes (dry, wet). Therefore, the assessment process has to deal with various uncertainties of the data. For the water use and also for possible emissions to water the climate and soil structure may need further attention in future works. There was a lack of reliable data especially for particle emissions of rock handling and storage, which seems to be an important emission source. Also most data concern U.S. production and only few data for Moroccan phosphate rock was available. In order to assess an representative average for world-wide phosphate mining also mines in China and the former soviet union should be included in future work.

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63 Phosphoric acid

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Last Changes:

2004

63.1 Introduction

After sulphuric acid, phosphoric acid is the most important mineral acid in terms of volume and value. This is mainly due to the enormous demand for wet phosphoric acid for further processing to fertilisers (Ullmann 2001b).

There are two different possibilities to produce phosphoric acid. The processes using phosphate minerals that are decomposed with an acid are known as wet process. The majority of phosphoric acid, approximately 96 %, is produced using the wet process method (EPA 1996). Wet process phosphoric acid is also used for fertiliser production. The other possibility is phosphoric acid production using a thermal process. This process needs a high amount of energy and produces strong phosphoric acid liquid (of about 85 wt-% of H_3PO_4) which is required for high grade chemical production (EPA 1996). In recent times concentrated phosphoric acid (ca. 85 wt-% of H_3PO_4) for high-grade chemical production is also produced by purification of fertiliser grade phosphoric acid. Most of the wet phosphoric acid produced world-wide is made with the dihydrate process (Ullmann 2001b). In this inventory only the phosphoric acid production with the dihydrate wet process was investigated, because it is the most common production process.

For this inventory the functional unit is 1 kg of H_3PO_4 . For fertiliser grade phosphoric acid a concentration of 70 wt-% H_3PO_4 was assumed. For the purified industrial grade phosphoric acid a concentration of 85 wt-% H_3PO_4 was used. The most important physical properties of phosphoric acid used in this inventory are given in Tab. 63.1.

Tab. 63.1 Chemical properties of phosphoric acid (Ullmann 2001b)

Property, element	Unit	Fertiliser grade	Industrial grade
		per kg acid	per kg acid
H_3PO_4 content	wt. %	70	85
Phosphorus as P_2O_5	wt. %	50.7	61.6
Specific gravity	$kg\ m^{-3}$ at 25 °C	1.57	1.69

Molecular weight of H_3PO_4 : 98 g mol⁻¹; P_2O_5 : 141.94 g mol⁻¹; P: 30.97 g mol⁻¹

63.2 Reserves and resources of material

For the production of wet phosphoric acid the most important resource is phosphate rock. For the digestion of the phosphate rock, large quantities of sulphuric acid are needed. In addition, a large amount of process water (internally recycled) is consumed. Due to the large quantities of phosphate rock and sulphuric acid needed, the plants are often built in vicinity of phosphate mines and on the same sites as sulphuric acid plants.

The U.S. is the largest producer of phosphoric acid (see Tab. 63.2). Approximately 65% of the U.S. phosphate rock processing capacity is located in Florida (Maene 1999). More than 90% of the U.S. phosphate rock ore produced was used to manufacture wet-process phosphoric acid and superphosphoric acid (Jasinski 2000).

Morocco is expanding its capacities for phosphoric acid strongly. Especially the phosphoric acid plants in Jorf Lasfar and Safi were expanded recently. There have been several plant closures in West

Europe, where phosphoric acid production capacity and output have fallen by 60% since 1980, for economic and environmental reasons (Maene 1999). For this inventory only the phosphoric acid production from Moroccan and U.S. (Florida) phosphate rock was investigated.

Tab. 63.2 World-wide phosphoric acid capacity in 1997 and forecast for 2002 (IFA as cited in Maene 1999)

Region	Capacity as P ₂ O ₅				Capacity as H ₃ PO ₄			
	1997		Forecast 2002		1997		Forecast 2002	
	Mt a ⁻¹	%	Mt a ⁻¹	%	Mt a ⁻¹	%	Mt a ⁻¹	%
North America	11.85	34	12.28	29	16.36	34	16.95	29
Central Europe & FSU	7.87	22	8.15	19	10.86	22	11.24	19
Africa	5.84	17	7.24	17	8.06	17	9.99	17
Asia (incl. China)	3.51	10	6.64	16	4.85	10	9.16	16
Near East	2.65	7	3.29	8	3.65	7	4.55	8
West Europe	1.88	5	1.90	5	2.59	5	2.62	5
Other countries	1.69	5	2.52	6	2.33	5	3.48	6
Total world	35.28	100	42.01	100	48.70	100	57.98	100

Data source: International fertiliser organisation (IFA).

63.3 Use of material / product

Phosphoric acid can be produced either in a thermal or a wet process. The purified wet-process phosphoric acid, which is less costly to produce than thermal acid, has attained a greater market share than thermal acid as raw material for industrial phosphorus derivatives (Hume et al., 2000). Approximately 96% of the phosphoric acid is produced using the wet process (EPA 1996). Purified wet-process phosphoric acid can be used to produce most phosphorus compounds except for phosphorus pentasulfide and phosphorus trichloride, which is used to make herbicides, pesticides, and flame-retardants.

The U.S. accounts for 40% of world trade of converted phosphate products (Demetriou 2001). More than 50% of the wet-process phosphoric acid produced in the U.S. was exported in the form of upgraded granular diammonium and monoammonium phosphate fertiliser (MAP, DAP), triple superphosphate fertilizer (TPM), and merchant grade phosphoric acid (Jasinski 2000).

63.4 Systems characterization

Because of different ore properties (dry and wet rock) and different ways of phosphogypsum disposal, two processes for phosphoric acid production were investigated. One is the phosphoric acid production in Morocco (dry rock), where the gypsum cake is slurried with seawater and discharged into the Atlantic Ocean. The other is the phosphoric acid production in USA (mainly Florida; with wet rock), where the gypsum cake is stacked. Stacking is by far the most popular phosphogypsum disposal method.

Disposal of phosphogypsum on land or to the sea accounts for about 98% of the production (Ullmann 2001b). Only a small part of phosphogypsum is commercially reused. The reason is the content of impurities such as heavy metals or radioactive elements. Because of the small amount of reused phosphogypsum this process path was neglected.

Within the phosphoric acid production, fluosilic acid is derived as co-product. Therefore, an allocation between the two products was made. The following processes were modelled:

- Phosphoric acid production, dihydrate process (location: US): Multi output process with phosphoric acid, fertilizer grade, 70% in H₂O, at plant (US) and fluosilicic acid, 22% in H₂O, at plant (US) as allocated products; see Fig.63.1.
- Phosphoric acid production, dihydrate process (location: MA): Multi output process with Phosphoric acid, fertilizer grade, 70% in H₂O, at plant (MA) and fluosilicic acid, 22% in H₂O, at plant (MA) as allocated products; see Fig.63.2.
- Phosphoric acid, fertilizer grade, 70% in H₂O, at plant (location: GLO); supply mix from U.S. and Moroccan production calculated.
- Fluosilicic acid, 22% in H₂O, at plant (location: RER); Supply mix from U.S. and Moroccan production calculated.
- Phosphoric acid, industrial grade, 85% in H₂O, at plant (location: RER); see Fig.63.3.
- Phosphoric acid plant, fertiliser grade (location: US); infrastructure process; see. Fig.63.4

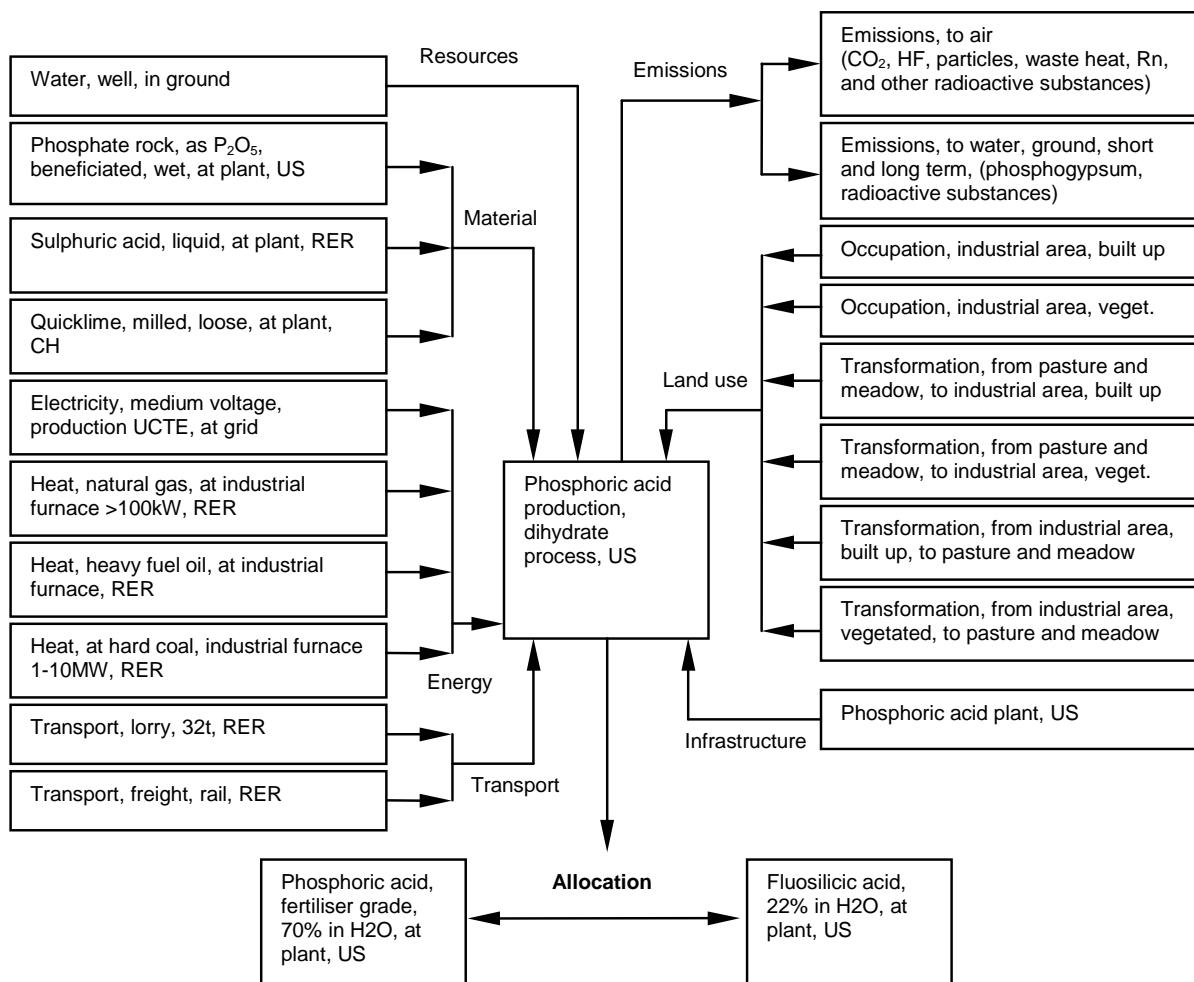


Fig.63.1 Process chain for the production of phosphoric acid (fertiliser grade) in the U.S. (Florida)

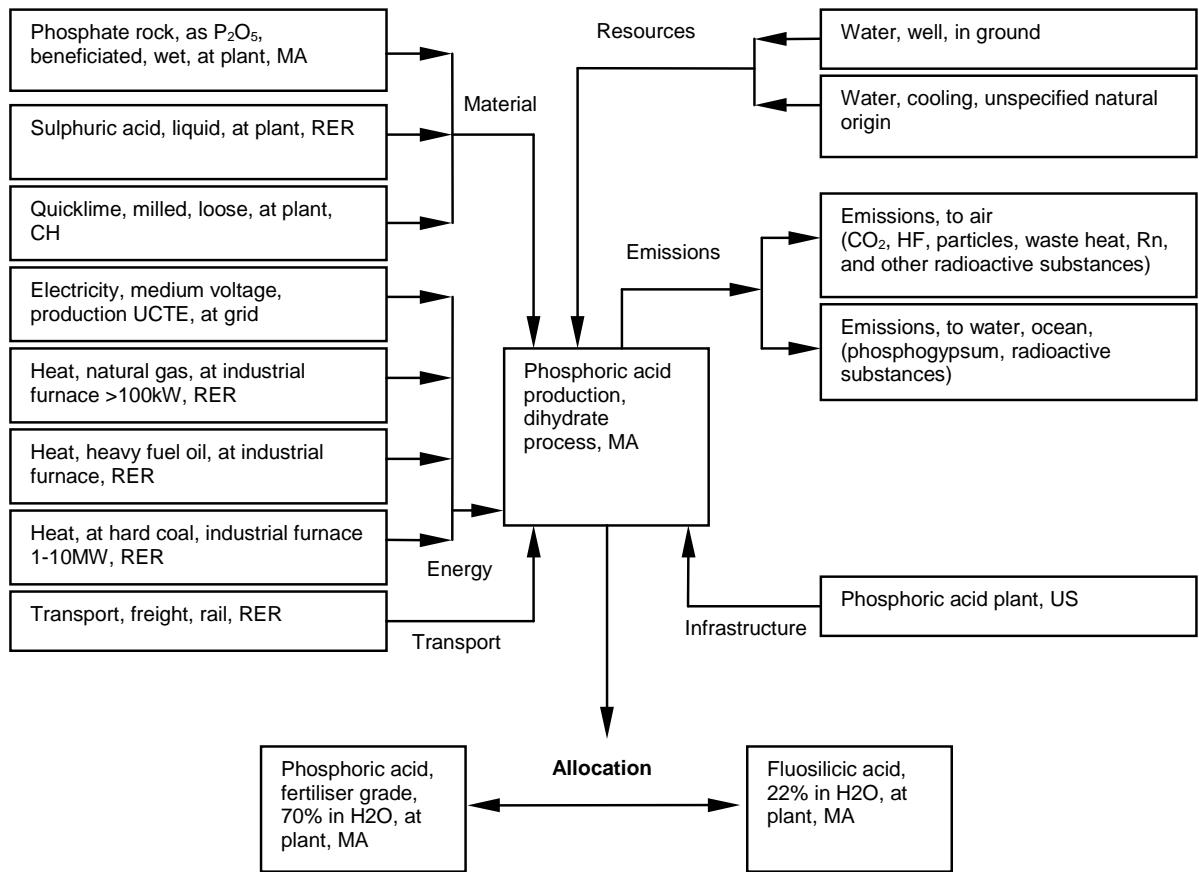


Fig.63.2 Process chain for the production of phosphoric acid, fertiliser grade in Morocco

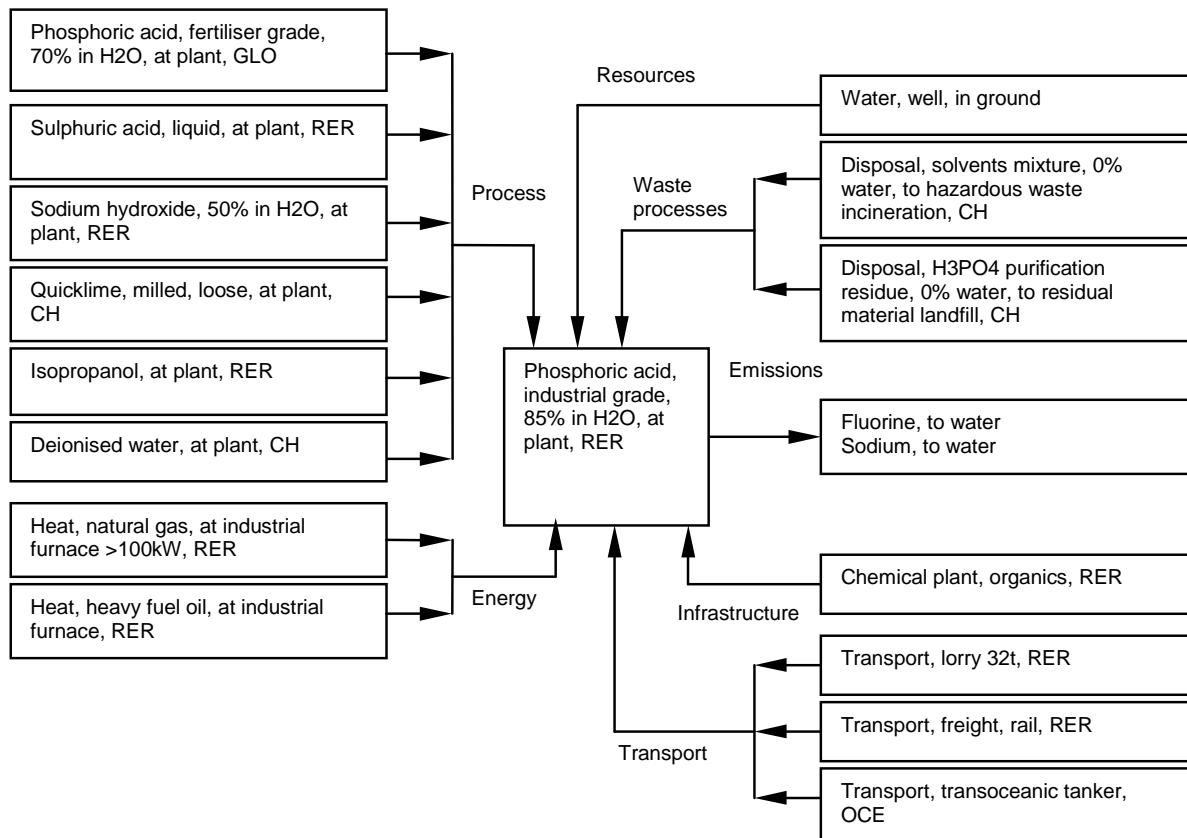


Fig.63.3 Process chain for the production phosphoric acid, industrial grade in Europe

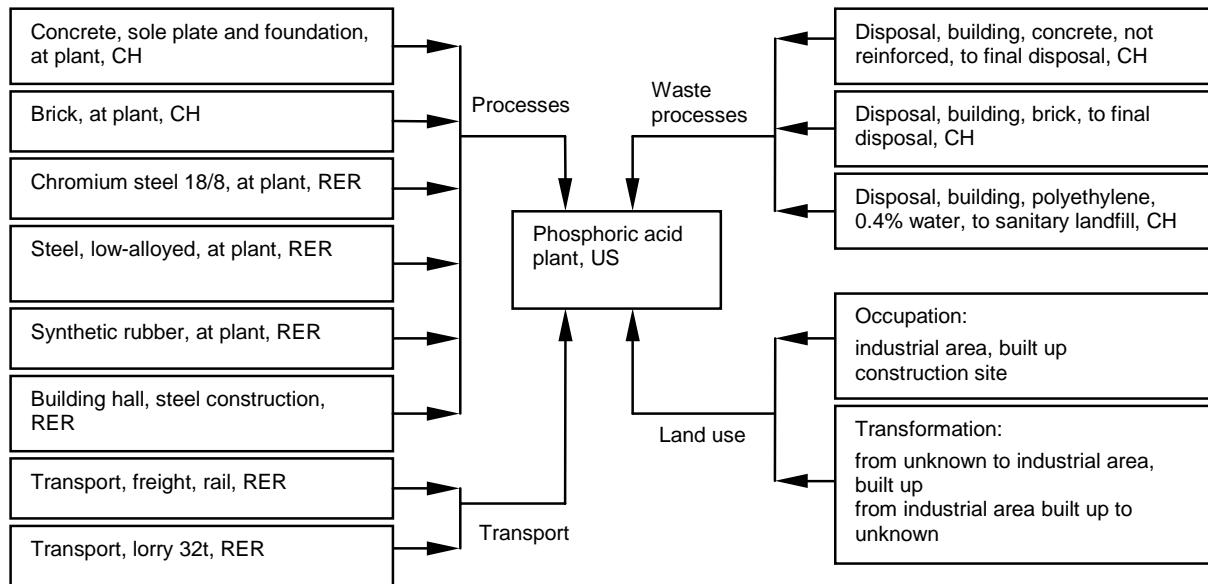


Fig.63.4 Process chain for the dihydratephosphoric acid plant (location US)

63.5 Phosphoric acid production, dihydrate process

63.5.1 Process

Wet-process phosphoric acid production is possible with either nitric-, hydrochloric- or sulphuric-acid. In this inventory only the process with sulphuric acid was concerned. This is the process normally used in the production of fertilisers in Europe (EFMA 1995). There are five types of phosphoric acid production routes with sulphuric acid. Some important characteristics of these processes are given in Tab. 63.3.

Most of the wet phosphoric acid produced world-wide is produced with the dihydrate process (Ullmann 2001b) (>80% of the capacity worldwide(Becker 1989, p.9)). Facilities in the U.S. generally use a dihydrate process (EPA 1996). Recently two production sites in the Netherlands were closed (1999/2000). These plants operated with a high efficiency and low emission hemihydrate recrystallisation process (HRC) or hemidihydrate process (HDH) respectively (Koopman 2001). This leads to a shift of phosphoric acid production to sites where production (mainly with the dihydrate process) is cheap and where the environmental laws are weaker. In this inventory only the dihydrate process route was considered because it is by far the most common.

Tab. 63.3 Characteristics of the different wet phosphoric acid production processes (Becker 1989)

Process	Acid concen-	Efficiency	Acid concen-	Phospho-
	tration	% P ₂ O ₅		gypsum quality
Dihydrate (DH)	28-30	94-96	required	impure
Hemihydrate (HH)	40-48	90-94	not required	impure
Hemihydrate recrystallisation (HRC)	30-32	97	required	pure
Dihemihydrate (DH / HH)	32-36	98	required	pure
Hemidihydrate (HDH)	40-52	98.5	not required	pure

In the dihydrate process, acid with a concentration of 28-30% P₂O₅ is obtained. Therefore, the crude acid has to be concentrated to obtain acid with a commercial concentration of 50-54% P₂O₅. The acid is usually concentrated to 50 wt-% P₂O₅ by using two or three vacuum evaporators (EPA 1996). During this concentration step about 50-60% of the fluorine content of wet phosphoric acid is volatilised. 90-95% of the generated fluorine can be converted to a 15-25% fluosilicic acid solution (H₂SiF₆). This acid is accounted as co-product of the process.

A simplified process scheme of phosphoric acid production with the dihydrate process is shown in Fig. 63.5.

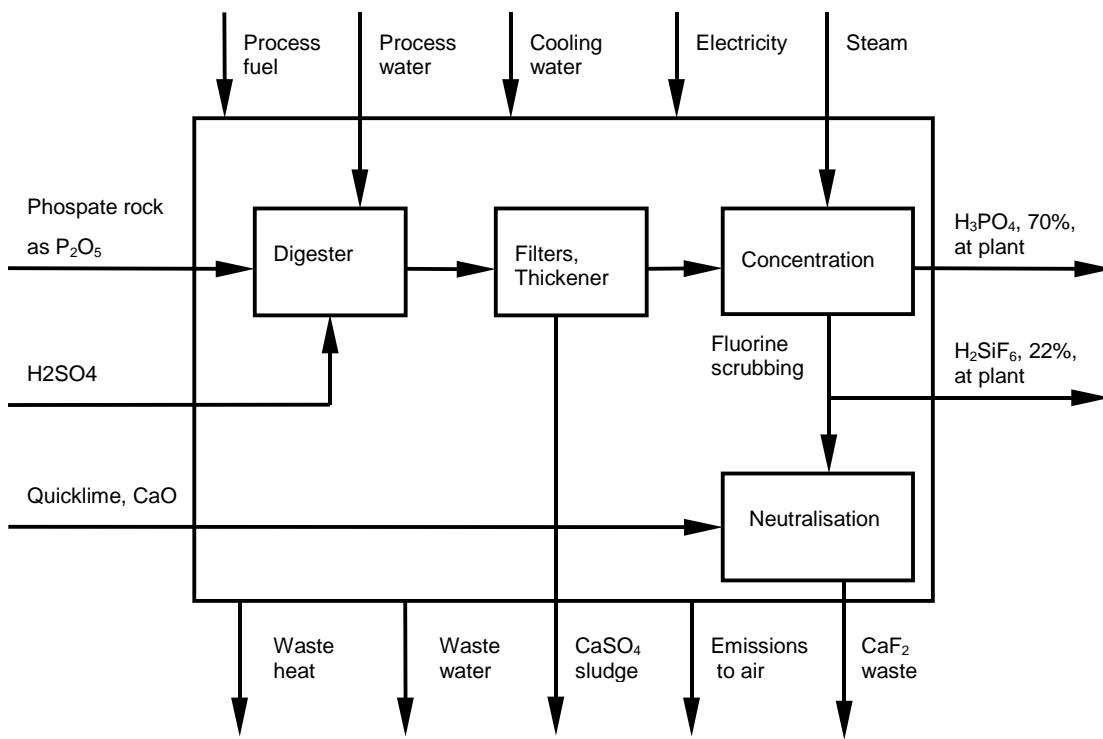


Fig. 63.5 Simplified process of phosphoric acid production, dihydrate process

The basic chemistry of the dihydrate process can be described as follows. The tricalcium phosphate in the phosphate rock is converted by reaction with concentrated sulphuric acid into phosphoric acid and the insoluble salt calcium sulphate (EFMA 1995). The reaction can be formulated simplified as follows:



63.5.2 Resources

Phosphate rock

According to the different sources investigated (see Tab. 63.4) the demand of phosphate rock (as P₂O₅) lies in the range of 1.04-1.06 kg P₂O₅ per kg P₂O₅ in the produced acid. This reflects the phosphate efficiency of the dihydrate process of 94-96%. For this inventory a difference was made between the phosphoric acid production with dry-rock in Morocco (33% P₂O₅) and with wet-rock in Florida (29% P₂O₅). According to Becker 1989, the efficiency is lower in the wet-process and also lower by using lower grade ore. Therefore, for the U.S. phosphoric acid a value of 1.06 kg P₂O₅ and for the Moroccan phosphoric a value of 1.04 kg P₂O₅ per kg P₂O₅ in the produced acid was used according to the data of Becker 1989.

Sulphuric acid

In general, a sulphuric acid concentration of 93-98 wt-% is used for the digestion of the phosphate rock. According to the different sources investigated (see Tab. 63.4) the demand of sulphuric acid lies in the range of 2.5-3 kg per kg P₂O₅ in the produced acid. According to data from Becker 1989, the demand depends on the source of phosphate rock (quality) and the processing type (dry-rock or wet-rock). By using an average value, most data sources investigated therefore report a value of 2.7-2.8 kg H₂SO₄ per kg P₂O₅ in the produced acid. For this inventory, a difference was made between the phos-

phoric acid production with dry-rock in Morocco and with wet-rock in Florida. Therefore, for the U.S. phosphoric acid a value of 3.06 kg H₂SO₄ and for the Moroccan phosphoric acid a value of 2.54 kg H₂SO₄ per kg P₂O₅ in the produced acid was used, according to the data of Becker 1989. For the values of the different data sources see Tab. 63.4.

Process- and cooling water

The consumption of process water depends mainly on the concentration of the weak acid obtained in the filter and whether the condensed water in the evaporation loop is returned to the process or not. The process water consumption reported is in the range of 4-7 kg per kg P₂O₅ (EFMA 1995). The values of the different sources are listed in Tab. 63.4. For the U.S. phosphoric acid, a value of 3.63 kg process water per kg P₂O₅ in the produced acid was used according to the data of Becker 1989 for wet rock production. For the Moroccan phosphoric acid, a value of 5.12 kg process water per kg P₂O₅ in the produced acid was used, according to the data of Landbank 1994, which describes the production plant in Safi (MO). Concerning the water resource, untreated water from a well was assumed.

The amount of cooling water varies from 37.5 kg (Büchel et al. 1999) to 100-150 kg (EFMA 1995) per kg of P₂O₅ in the acid. From the different sources it was not clear which values represent the water make up or the amount of circulating water. According to Becker 1989, the circulating cooling water for the concentration of the acid amounts to 100 kg per kg of P₂O₅. The amount of cooling water also depends largely on the type of cooling system used. Especially for plants operating with cooling ponds and water recycling, such as in Florida, the water make up needed largely depends on the amount of rainfall. Plants in Florida (1370 mm rain per year) can operate with a balanced water management (Becker 1989). For the U.S. phosphoric acid plants no additional cooling water demand was therefore assumed. According to Landbank 1994, the cooling water demand is primarily used for the acid concentration step. An amount of 71 kg per kg P₂O₅ (51.4 kg per kg H₃PO₄) in the acid was reported. This amount was used as cooling water demand in the inventory for Moroccan phosphoric acid where no cooling pond system is operated. The water used in those plants origins from the sea (Landbank 1994).

Other resources

There were only few data available on the process demands of further materials and resources. According to Mc Ketta & Cunningham 1990, 0.114 kg quicklime (as 100% CaO) and 0.001 kg antifoam is needed per kg P₂O₅ in the acid. In this inventory only the quicklime was considered. It is used for neutralising the fluorine containing scrubbing liquor. There was no information available about the type of antifoam used. Because of the small amount used and the missing data, it was neglected in this inventory.

Tab. 63.4 Resources for phosphoric acid production. Selected values for this inventory

Rock type, % P ₂ O ₅	Amount per kg P ₂ O ₅ in acid			Amount per kg H ₃ PO ₄ in acid		
	Phosphate rock	Sulphuric acid	Process water	Phosphate rock	Sulphuric acid	Process water
	kg P ₂ O ₅	kg H ₂ SO ₄	kg H ₂ O	kg P ₂ O ₅	kg H ₂ SO ₄	kg H ₂ O
Dry rock, 36.7%, ¹	1.04	2.54	3.42	0.753	1.84	2.48
Dry rock, 28.8%, ¹	1.05	3.01	3.75	0.760	2.18	2.72
Wet rock, 28.8%, ²	1.06	3.06	3.63	0.768	2.22	2.63
Dry rock, 34%, ³	1.05	2.78	5.12	0.760	2.01	3.71
Unspecified, ⁴	1.04 - 1.06	-	4 - 7	0.75-0.77	-	2.90-5.07
Average, 32%, ⁵	1.05	2.70	-	0.760	1.96	-
Unspecified, ⁶	1.05	2.80	7.0	0.760	2.03	5.07
Unspecified, ⁷	1.06	3.00	5.1	0.768	2.17	3.69
Dry rock, 33%, ⁸	1.04	2.54	5.12	0.753	1.84	3.71
Wet rock, 29%, ⁹	1.06	3.06	3.63	0.768	2.22	2.63

¹ Material balance for dry-rock process. Data source: (Becker 1989; Fig. 2.1, Fig. 2.2).

² Material balance for wet-rock process. Data source: (Becker 1989; Fig. 2.3). Wet-rock with 28.8% P₂O₅; 38% water content of rock feed. Process water amount without rock water content: 1.55 kg H₂O per kg P₂O₅ in acid.

³ Data source: (Landbank 1994). Phosphate rock assumed with a concentration of 34 wt-% P₂O₅. 3.08 kg rock needed per kg P₂O₅ in acid.

⁴ Data source: (EFMA 1995). P₂O₅ efficiency 94- 96%. 2.6 – 3.5 kg rock needed per kg P₂O₅ in acid.

⁵ Data source: (Patyk & Reinhardt 1997). Average of 80% dihydrate process (50% wet-rock, 50% dry rock), 20% hemihydrate process.

⁶ Data source: (Büchel et al. 1999). P₂O₅ efficiency 95%. 3.45 kg rock needed per kg P₂O₅ in acid.

⁷ Data source: (Mc Ketta & Cunningham 1990). 3.45 kg rock with 30% P₂O₅ needed per kg P₂O₅ in acid.

⁸ Values used for Moroccan phosphoric acid production using dry-rock as phosphate source.

⁹ Values used for U.S. (Florida) phosphoric acid production using wet-rock as phosphate source.

Process energy

A phosphoric acid plant requires electric power and steam to operate the process. The power consumption depends on whether the process requires the grinding of the phosphate rock or not. According to (EFMA 1995) the electricity consumption is about 120-180 kWh per ton P₂O₅ in the acid. Other sources show with 92 kWh per ton P₂O₅ lower values (Mc Ketta & Cunningham 1990) or with 301 kWh per ton P₂O₅ also much higher values (Landbank 1994). For this inventory the average value of 191 kWh per ton P₂O₅ reported for the U.S. phosphoric acid industry (IFA 2000a) was used. The same value was used for dry and wet rock processes.

Steam is used mainly for the concentration of the dilute crude acid. According to EFMA 1995, about 0.5-2.2 kg steam per kg P₂O₅ in the acid are needed. The lower value refers to the hemihydrate process and the higher to the dihydrate process. The values given in Patyk & Reinhardt 1997 with about 3-3.5 kg steam per kg P₂O₅ (8.3-9.6 MJ) seem too high. For the values of the different data sources see Tab. 63.5. As value used in this inventory, the average of the values for the dihydrate process was taken, excluding the values given by Patyk & Reinhardt 1997. This lead to a heat demand of 5.5 MJ per kg P₂O₅ in the acid. When the phosphoric acid plant is linked to a sulphuric acid plant, excess low pressure steam from the sulphuric acid plant is used for phosphoric acid vacuum concentration (EFMA 1995). There was no data available about to which extend such steam is used in the different locations.

In OIT 2000 a splitting of the energy used for heat and steam in phosphoric acid production is presented. This splitting refers to the total fertiliser industry and not only to the phosphoric acid plants. Because no other data was available, this split was used in this inventory. According to OIT 2000, 77% of the energy origins from natural gas, 3% from fuel oil or LPG, 10% from coal, and 10% from

other sources such as purchased steam or renewables in the USA. For this inventory, 4.23 MJ per kg P₂O₅ (3.06 MJ per kg H₃PO₄) were accounted as heat from a natural gas furnace, 0.17 MJ per kg P₂O₅ (0.12 MJ per kg H₃PO₄) as heat from a heavy fuel oil furnace and 0.55 MJ per kg P₂O₅ (0.4 MJ per kg H₃PO₄) as heat from a coal furnace. The share for “other sources” (0.55 MJ kg⁻¹ P₂O₅) was not accounted because it was assumed that this amount originates from steam of a sulphuric acid plant, which bears no burden within the methodology of this inventory.

Tab. 63.5 Energy resources for phosphoric acid production. Selected values for this inventory

Rock type, % P ₂ O ₅	Amount per kg P ₂ O ₅ in acid			Amount per kg H ₃ PO ₄ in acid		
	Electricity	Steam	Heat	Electricity	Steam	Heat
				kWh	kg	MJ
Average U.S., -, ¹	0.191	-	-	0.138	-	-
Dry rock, 34%, ²	0.301	-	4.71	0.218	-	3.41
Unspecified, ³	0.12 - 0.18	0.5 - 2.2	(1.38-6.05)	0.09-0.13	0.36-1.59	(1.0-4.38)
Average, 32%, ⁴	0.19	-	8.33 - 9.59	0.138	-	6.03-6.94
Unspecified, ⁵	0.12	2	(5.5)	0.087	1.45	(3.98)
Unspecified, ⁶	0.09	2.87	(7.89)	0.065	2.08	(5.71)
Unspecified, ⁷	0.29	-	4.3	0.210	-	3.11
Dry rock, 33%, ⁸	0.191	-	5.5, ¹⁰	0.138	-	3.98, ¹⁰
Wet rock, 29%, ⁹	0.191	-	5.5, ¹⁰	0.138	-	3.98, ¹⁰

Applied conversion factor for Steam: 2.75 MJ heat per kg Steam (values in brackets)

¹ Data source: (IFA 2000a). Average for U.S. industry in 1995.

² Data source: (Landbank 1994). Thereof 76% used in the dihydrate process and 24% in the concentration step.

³ Data source: (EFMA 1995). higher value dihydrate process, lower value hemihydrate process.

⁴ Data source: (Patyk & Reinhardt 1997). Average of 80% dihydrate process, 20% hemihydrate process.

⁵ Data source: (Büchel et al. 1999). Value for dihydrate process

⁶ Data at source: (Mc Ketta & Cunningham 1990). Value for dihydrate process

⁷ Data source: (OIT 2000). Final energy demand for steam / process heat of 4.78 MJ per kg P₂O₅ in acid. Assumed efficiency of conversion to heat 90%.

⁸ Values used for Moroccan phosphoric acid production using dry-rock as phosphate source.

⁹ Values used for U.S. (Florida) phosphoric acid production using wet-rock as phosphate source.

¹⁰ Amount of heat for steam refers to a production of concentrated acid (concentration ca. 70% H₃PO₄). Split of heat sources (natural gas, fuel oil, coal, and steam from sulphuric acid plant) according to data from (OIT 2000).

63.5.3 Products of the process and used unit processes

Products

The main product is phosphoric acid with a commercial concentration of about 50% P₂O₅. Fluosilicic acid with a concentration of about 22% H₂SiF₆ is obtained as a co-product. The quantity of 100% fluosilicic acid produced depends on the composition of the phosphate rock used. In general, it is in the range of 20-30 kg per ton P₂O₅ in the produced acid (EFMA 1995).

Tab. 63.6 Typical fluorine distribution for the phosphoric acid dihydrate process (Ullmann 2001b)

Fluorine distribution	in %	in kg F per kg P ₂ O ₅ produced	
		U.S. Production ¹	Moroccan Production ²
Phosphate rock feed	100	135 * 10 ⁻³	117 * 10 ⁻³
Phosphoric acid with 50% P ₂ O ₅	15	20 * 10 ⁻³	18 * 10 ⁻³
Phosphogypsum	43	58 * 10 ⁻³	50 * 10 ⁻³
Reactor off-gas	5	7 * 10 ⁻³	6 * 10 ⁻³
Flash cooler vapour	2	3 * 10 ⁻³	2 * 10 ⁻³
Concentrator vapour	35	47 * 10 ⁻³	41 * 10 ⁻³

¹ Assuming 3.7 wt-% fluorine in the phosphate rock and a demand of 3.66 kg rock per kg P₂O₅ in the acid.

² Assuming 3.7 wt-% fluorine in the phosphate rock and a demand of 3.15 kg rock per kg P₂O₅ in the acid.

According to the fluorine distribution shown in Tab. 63.6, up to 57 kg fluorine in the produced acid per ton P₂O₅ could be removed from the vapour (reactor off-gas, flash cooler and concentrator vapour). Some of the fluorine containing scrubbing liquor is disposed of after neutralisation with lime or limestone (EFMA 1995). Another part can be recovered as dilute fluosilic acid. For this inventory it was assumed that in average an amount of 25 g fluosilic acid (100%) per kg P₂O₅ (or 20 g F per kg P₂O₅) is used as co-product. Calculated per kg H₃PO₄ in the acid, this leads to an amount of 18 g fluosilic acid (100%).

Used processes

For all electricity demands the process “electricity, medium voltage, production UCTE, at grid” was assumed. For heat production the processes “heat, natural gas, at industrial furnace >100kW, RER”, “heat, heavy fuel oil, at industrial furnace, RER”, and “heat, at hard coal industrial furnace 1-10MW, RER” were used. Besides the resources “phosphate rock, as P₂O₅, beneficiated, wet, at plant, US” and “phosphate rock, as P₂O₅, beneficiated, dry, at plant, MA” the processes “sulphuric acid, liquid, at plant, RER” and “quickslime, milled, loose, at plant, CH” were used for the process inputs.

63.5.4 Emissions to air

CO₂ emissions

The CO₂ in the phosphate rock is released during the digestion of the rock. According to data of phosphate rocks from 16 different mines (Becker 1989), an average content of 3.7% CO₂ in U.S. phosphate rock and 5.6% in Moroccan phosphate rock was calculated (weighted average). According to (Becker 1989), the CO₂ in the rock is not emitted if wet-rock is processed. For the dry-rock stoichiometric CO₂ emissions can be assumed. Therefore, CO₂ emissions are only released in the Moroccan phosphoric acid process. The emission was calculated as 0.176 kg CO₂ per kg P₂O₅ in the acid (33% P₂O₅ in the phosphate rock). Further CO₂ emissions (and also CO-, SO₂, NO_x and other emissions) caused by the burning of fuel for steam generation are included in the linked furnace processes and, therefore, need no further attention here.

Fluorine emissions

Data concerning fluoride emissions to air were calculated with the emission factors presented in EPA 1993b. Scrubbers are commonly used for emission control. The controlled emissions reported for the reactor, evaporator, and the filtration are 2.3 mg per kg P₂O₅. The values presented in Landbank 1994 for fluoride emissions to air are with 69 mg per kg P₂O₅ about 30 times higher than the controlled emissions according to EPA 1993b. The uncontrolled emissions according to EPA 1993b amount to 231 mg per kg P₂O₅. According to the values for EFMA emission limits presented in IFA 2000b, the

fluorine emissions should not be higher than 40 mg per kg P₂O₅ (or 5 mg Nm⁻³) for a new plant and 240 mg per kg P₂O₅ for an old plant¹⁹ (or 30 mg Nm⁻³). According to those limit values the emission factors for controlled emission given in EPA 1993b seem very low. As an average, the value given in Landbank 1994 was assumed for both locations (U.S, MA) in this inventory.

There was little information available on fluorine emission factors for the phosphogypsum stacks. It is stated that the emissions are very site specific (Becker 1989,EPA 1993b). According to Ball et al. 1999, the fluorine emissions from the stacks split between hydrogen fluoride (HF) and silicon tetra-fluoride (SiF₄), with a ratio of about 50% / 50%. The split of the emissions may vary to a large extend (20-61% HF emissions) and is therefore uncertain. An emission factor for fluoride emissions from stacks is given in Cargill Fertilizer 1999. This factor quantifies an emission of 1.3 kg fluorine per km² stack area and per day. Assuming gypsum stacks, a cooling pond area (land transformation) of 156 *10⁻⁶ m² per kg P₂O₅, and an emission time of 100 years, an amount of 8 mg F per kg P₂O₅ is calculated.

Particulate emissions

Data on the particulate emissions within the phosphoric acid production were scarce. Total particulate emissions (TPM) from phosphoric acid process equipment, measured for 1 digester and 1 filter, is reported in EPA 1993b. The digester produces as much as 5.5 g TPM per kg P₂O₅ and the filter releases approximately 0.1 g TPS per kg P₂O₅. Of this particulate, 3- 6% were fluorides. It is not stated if those emissions include any emission control. According to data measured within the normal superphosphate production (EPA 1993a), the controlled particulate emissions account for 0.28 g TPM per kg P₂O₅ for the rock unloading, 0.06 g TPM per kg P₂O₅ for the rock feeding, and 0.26 g TPM per kg P₂O₅ for the mixer and conveyor. Further, 3.6 g TPM per kg P₂O₅ of uncontrolled emissions are released in the curing storage. This process step is not comparable to the phosphoric acid production. For this inventory the values for controlled particulate emissions for rock unloading, rock feeding, and the mixer were taken from the normal superphosphate production. This leads to total particulate emissions of 0.6 g TPM per kg P₂O₅. According to the data of EPA 1993a, the value for PM10 emissions for those production steps accounts to 0.4 g PM10 per kg P₂O₅.

Further, particulate emissions occur on the phosphogypsum storage stacks due to wheel traffic and wind erosion. According to Berish 1990, the estimated annual dust emissions for Florida phosphogypsum stacks amounts to 19.7 t per year. Taking into account the yearly acid production in Florida of about 8 Mt P₂O₅ per year, those dust emissions are negligible.

According to the values for EFMA emission limits presented in IFA 2000b, the particle emissions should not be higher than 50 mg Nm⁻³ (or 0.4 g per kg P₂O₅)²⁰ for a new plant and 150 mg Nm⁻³ (or 1.2 g per kg P₂O₅) for an old plant. For this inventory an amount of 0.6 g TPM per kg P₂O₅ was applied as average emission value. The uncertainty of these values is high due to the weak data.

There were no actual and reliable information available on the particle distribution of the phosphoric acid production. For particle emissions from material handling operations, the distribution was estimated with data for rock screening and handling as presented in CEIDARS 2000; ID 37. For PM 2.5 the value given is 15% and for PM 10 it is 50% of the TPM value. This values correspond with the distribution (TPM, PM10) given in (EPA 1993a) for rock unloading and rock feeding in normal superphosphoric production. For the mixing and digesting operation, a PM 10 amount of 85% of the

¹⁹ Same conversion factor applied as for fluorine emissions limits of new plants (8 Nm³ per kg P₂O₅) presented in IFA 2000b
IFA (2000b) Mineral Fertilizer Production and the Environment. Part 2. Environmental Management Systems.
Technical Report No. 26. International Fertilizer Industry Association (IFA), Paris as pdf-File under: <http://www.agrifood-forum.net/publications/documents/tr26-part2.pdf..>

²⁰ Same conversion factor applied as for fluorine emissions limits of new plants (8 Nm³ per kg P₂O₅) presented in IFA 2000b
Ibid..

TPM value is reported. For this operation the particle size distribution for PM 2.5 was approximated with the values for fertiliser production given in Lükewille et al. 2001. PM 2.5 emissions are reported to be 65-70% of the PM 10 value. For this inventory the following distribution was calculated for the total process: 35% for > 10 µm, 39% for 2.5-10 µm and 26% for < 2.5 µm particle size. The values used are presented in Tab. 63.7.

Tab. 63.7 Phosphoric acid production. Emissions to air for Moroccan and U.S. (Florida) production

Emission, process	Unit	Moroccan production		U.S. (Florida) production	
		per kg H₃PO₄	per kg P₂O₅	per kg H₃PO₄	per kg P₂O₅
Waste heat, from electricity	MJ	0.498	0.688	0.498	0.688
CO ₂ , from digestion, ¹	kg	0.125	0.173	no	no
Fluorine, from process, as HF, ²	kg	50 * 10 ⁻⁶	69 * 10 ⁻⁶	50 * 10 ⁻⁶	69 * 10 ⁻⁶
HF, from gypsum storage, cooling ponds, short term, ³	kg	no stack	no stack	2.9 * 10 ⁻⁶	4 * 10 ⁻⁶
SiF ₄ , from gypsum storage, cooling ponds, short term, ³	kg	no stack	no stack	3.6 * 10 ⁻⁶	5 * 10 ⁻⁶
Particle (TPM), from rock unloading and processing ⁴	kg	0.43 * 10 ⁻³	0.6 * 10 ⁻³	0.43 * 10 ⁻³	0.6 * 10 ⁻³
Particle distribution⁸					
Particle, > 10 µm, total	kg	0.15 * 10 ⁻³	0.21 * 10 ⁻³	0.15 * 10 ⁻³	0.21 * 10 ⁻³
Particle, 2.5-10 µm, total	kg	0.17 * 10 ⁻³	0.23 * 10 ⁻³	0.17 * 10 ⁻³	0.23 * 10 ⁻³
Particle, > 2.5 µm, total	kg	0.12 * 10 ⁻³	0.16 * 10 ⁻³	0.12 * 10 ⁻³	0.16 * 10 ⁻³

¹ Emissions from released CO₂ during digestion of rock. Occurs only in dry-rock processing (Becker 1989).

² Fluoride emissions from reactor, evaporator, filter. Source: (Landbank 1994), counted as HF.

³ Values for fluoride emissions of stack and cooling ponds 50% as HF, 50% as SiF₄. Source: (Cargill Fertilizer 1999).

⁴ Values for dust emissions of normal superphosphoric acid plant, rock handling and acid mixer (EPA 1993a).

⁸ Calculated from particle distribution of the different emission sources.

Waste heat to air

To calculate the waste heat to the air, it was assumed that 100% of the waste heat from electricity use is emitted to air. This seems reasonable because mainly motors and other air-cooled equipment use electricity. The waste heat of the fuel use is already included in the fuel processes (fuel in furnace) and therefore not considered here. There were 0.688 MJ per kg P₂O₅ waste heat to air accounted for in this inventory.

Emissions from radioactive substances

For the emissions from radioactive substances to air see chapter 63.5.5.

63.5.5 Emissions from radioactive substances

To estimate the radioactive emissions to air and water, values for typical installations from UNSCEAR 2000 were used in the calculations. No distinction between Moroccan and U.S. production was made because the values already varied largely within one plant due to different rock qualities or other production characteristic (Hull & Burnett 1996, Azouazi et al. 2001). For the calculation of the values specified per ton of ore throughput given in UNSCEAR 2000, an average ore concentration of 31% and an amount of 3.4 kg phosphate rock per kg P₂O₅ in the acid was used. For the U.S. (Florida) production, it was assumed that the reported emissions to water occur to 0.05% within short-term range and 99.95% in long-term range (see chapter 63.5.6). The reason is that the phosphogypsum waste is stacked and therefore emitted only within a longer time period to water (assumption that 0.005% of the gypsum is emitted in the short term and 10% in the long term). The values used for the inventory are presented in Tab. 63.8.

Tab. 63.8 Phosphoric acid production. Radioactive emissions to air and water.

Substance, Path	Unit	Moroccan production		U.S. (Florida) production	
		per kg H₃PO₄	per kg P₂O₅	per kg H₃PO₄	per kg P₂O₅
²³⁸ U, to air, low population	kBq	2.46E-04	3.40E-04	2.46E-04	3.40E-04
²²⁸ Th, to air, low population	kBq	7.04E-06	9.71E-06	7.04E-06	9.71E-06
²²⁶ Ra, to air, low population	kBq	3.17E-04	4.37E-04	3.17E-04	4.37E-04
²²² Ra, to air, low population	kBq	2.89E+00	3.98E+00	2.89E+00	3.98E+00
²¹⁰ Pb, to air, low population	kBq	2.82E-04	3.89E-04	2.82E-04	3.89E-04
²¹⁰ Po, to air, low population	kBq	4.93E-04	6.80E-04	4.93E-04	6.80E-04
⁴⁰ K, to air, low population	kBq	2.82E-05	3.89E-05	2.82E-05	3.89E-05
²³⁸ U, to water, ¹	kBq	1.18E+00	1.63E+00	5.91E-04	8.16E-04
²³⁸ U, to water, long term, ²	kBq			1.18E+00	1.63E+00
²²⁸ Th, to water, ¹	kBq	2.82E-02	3.89E-02	1.41E-05	1.94E-05
²²⁸ Th, to water, long term, ²	kBq			2.81E-02	3.88E-02
²²⁶ Ra, to water, ¹	kBq	2.59E+00	3.58E+00	1.30E-03	1.79E-03
²²⁶ Ra, to water, long term, ²	kBq			2.59E+00	3.58E+00
²¹⁰ Pb, to water, ¹	kBq	2.30E+00	3.18E+00	1.15E-03	1.59E-03
²¹⁰ Pb, to water, long term, ²	kBq			2.30E+00	3.17E+00
²¹⁰ Po, to water, ¹	kBq	3.51E+00	4.84E+00	1.75E-03	2.42E-03
²¹⁰ Po, to water, long term, ²	kBq			3.51E+00	4.84E+00
⁴⁰ K, to water, ¹	kBq	2.78E-01	3.84E-01	1.39E-04	1.92E-04
⁴⁰ K, to water, long term, ²	kBq			2.78E-01	3.84E-01

¹ All emissions to the ocean from the Moroccan plant. Short-term emissions to the groundwater from the U.S. plant (0.05% of total)

² Long-term emissions to groundwater in the U.S. plant. 99.95% of total emissions accounted as long-term emissions.

63.5.6 Phosphogypsum waste, as emissions to water

The most important waste from phosphoric acid production is the phosphogypsum produced. According to Becker 1989, Fig. 2.2 and 2.3, the amount of phosphogypsum depends on the P₂O₅ concentration of the rock feed. For a dry rock with 36.7% P₂O₅ an amount of 4.49 kg gypsum per kg P₂O₅ and for a wet rock with 28.8% P₂O₅ an amount of 5.66 kg gypsum per kg P₂O₅ is reported. For the Moroccan production (Landbank 1994) a value of 4.83 kg gypsum per kg P₂O₅ is reported (1.4 kg per kg acid with 29% P₂O₅). Also other sources give similar numbers for the amount of phosphogypsum:

(Ullmann 2001b) 4.5-5.5 kg gypsum per kg P₂O₅; (EFMA 1995) 5 kg gypsum per kg P₂O₅. For this inventory a value of 4.83 kg gypsum per kg P₂O₅ (Landbank 1994) was used for the Moroccan plant and a value of 5.66 kg gypsum per kg P₂O₅ (Becker 1989) was used for wet-rock processing in the U.S. phosphoric acid plant. Further, a small amount of CaF₂ is released from the neutralisation of fluorine (as SiF₄, HF, and H₂SiF₆). This amount is in the order of about 0.16 kg per kg P₂O₅.

Since the composition of the input and of the phosphoric acid were known (Tab. 1.4), the composition of phosphogypsum could be calculated by closing the mass balance. Of the P₂O₅ in the rock, 6% for the U.S. plants and 4% for the Moroccan plants are transferred to the phosphogypsum. For calcium and sulphate the transfer coefficients to phosphogypsum were calculated using the composition of an average crude acid given in Ullmann 2001b. This leads to a transfer coefficient to the gypsum of 99% for calcium and 97% for sulphate. For the value given in Tab. 45.4, the amount of quicklime used for neutralisation of the scrubbing liquor was added. The coefficient used for fluorine bases on a mass balance using the shares in Tab. 63.6 (Source: Ullmann 2001b) and taking 20 g F per kg P₂O₅ as co-product fluosilic acid into account. This leads to a transfer coefficient to the gypsum of about 70% for fluorine. To calculate the amount of trace elements (heavy metals) the concentration values stated in the inventory for Moroccan and U.S. phosphate rock (Althaus et al. 2003, based on data from Becker 1989) were used. The percentage share of these elements in the phosphogypsum was assessed with data given in Ullmann 2001b, Tab. 2. For arsenic and lead the transfer coefficient was roughly calculated using the composition of an average crude acid given in Ullmann 2001b. The average of the given range was used in this inventory. With these calculations, the values presented in Tab. 45.4 were calculated. These values were used to calculate the emissions to water.

U.S phosphoric acid plant

The phosphogypsum in U.S. (Florida) phosphoric acid plants is discharged from the filter, mixed with process water, and pumped to the decantation basins. In these basins the gypsum settles while the process water flows over into a cooling basin before being recycled to the plant. No direct water discharge was assumed due to the closed water circuit. As emissions, only leaching to surface aquifers were considered. The determination of those leachate rates is uncertain and bases on a rough interpretation of a phosphogypsum stack model presented in Nifong 1998. The water budget analysis in this model states that 50% of the rainfall on the gypsum storage area is infiltrated into the stack (the rest evaporates). With the ditch drainage 98% of the infiltrated water is collected. This means that 1% of the rain falling onto the stack area leaches into the aquifer. For the plants running with closed water circuit, as concerned in this case, there were no data on other water emissions reported.

The share of 1% leaching was used for the calculation of the short-term water emissions. For the calculation, a land use (transformation) for the gypsum stacks and the cooling ponds of $156 * 10^6 \text{ m}^2$ per kg P₂O₅ was assumed (see chapter 63.5.7). Assuming an amount of 1370 mm rain per year for Florida (Becker 1989) and a gypsum (calcium sulphate) solubility of 2.4 kg m⁻³ (Ullmann 2001b) this leads to the leaching of 5 mg gypsum per kg P₂O₅ and year. Accounting the time until the reclamation is completed to the short-term emission range, a leached amount of 0.33 g gypsum per kg P₂O₅ is calculated (using a land occupation of $10 * 10^{-3} \text{ m}^2$ a per kg P₂O₅). This amount accounts to 0.005% of the total amount of gypsum stored.

For the long-term emissions it was assumed that all infiltrated water (50% of the rain falling onto the site) would leach into the ground, because the ditch drainage is no longer operated after the end of the assumed 50 years reclamation time. Accounting a time frame of 10'000 years, this leads to a leaching of 0.26 g gypsum per kg P₂O₅ and year or 2.6 kg gypsum per kg P₂O₅ for the whole time period. This amount accounts to 45% of the total amount of gypsum stored. According to the calculations, 100% of the gypsum would be leached after 22'000 years. In a study of Seijdel 1999 leaching of phosphogypsum from the landfill was estimated to be 1% in the favourable case and 10% in unfavourable case.

For this inventory, an amount of 10% of the phosphogypsum (and all incorporated substances) was assumed for the long-term emissions to water. As limits for the uncertainty assessment the values of 1%

(low value) and 100% (high value) were used. The applied values for the composition of the phosphogypsum (substances considered within emission calculation) are given in Tab. 45.4. From these values, 0.005% were considered to be emitted to the water in the short-term and 10% in the long-term (see above). For the applied values see summary table in Section 63.11.

Moroccan phosphoric acid plant

Phosphoric acid plants in Morocco dispose the phosphogypsum directly to the sea where it dissolves rapidly due to the high solubility of gypsum. For this case 100% emission of the substances contained in the phosphogypsum were accounted as short-term emissions to seawater. The applied values for the composition of the phosphogypsum (substances considered as emission) is given in Tab. 63.9.

The applied values for the composition of the phosphogypsum (substances considered within the emission calculation) are given in Tab. 63.9. The resulting emissions from the Moroccan production were considered as short-term emissions to the ocean.

Tab. 63.9 Phosphoric acid production. Phosphogypsum composition.

Composition in kg	Coeff. ¹ %	Moroccan production		Coeff. ¹ %	U.S. (Florida) production	
		per kg H ₃ PO ₄	per kg P ₂ O ₅		per kg H ₃ PO ₄	per kg P ₂ O ₅
CaO, as Ca ⁺⁺ , ²	99	0.883	1.22	99	0.940	1.30
SO ₃ , as SO ₄ ²⁻	97	1.75	2.41	97	2.11	2.91
P ₂ O ₅ , as PO ₄ ³⁻	4	38.8 * 10 ⁻³	53.5 * 10 ⁻³	6	58.2 * 10 ⁻³	80.3 * 10 ⁻³
F, as F ⁻	69, ³	9.1 * 10 ⁻³	12.6 * 10 ⁻³	70, ³	4.2 * 10 ⁻³	5.8 * 10 ⁻³
Cd	20	19.0 * 10 ⁻⁶	26.2 * 10 ⁻⁶	20	30.8 * 10 ⁻⁶	42.5 * 10 ⁻⁶
Pb, ⁴	83	2.6 * 10 ⁻⁶	3.5 * 10 ⁻⁶	83	3.0 * 10 ⁻⁶	4.1 * 10 ⁻⁶
As, ⁴	14	50.2 * 10 ⁻⁶	69.3 * 10 ⁻⁶	14	14.8 * 10 ⁻⁶	20.5 * 10 ⁻⁶
Cr	8	5.6 * 10 ⁻⁶	7.8 * 10 ⁻⁶	8	1.9 * 10 ⁻⁶	2.6 * 10 ⁻⁶
Cu	6	6.2 * 10 ⁻⁶	8.6 * 10 ⁻⁶	6	72.7 * 10 ⁻⁶	100 * 10 ⁻⁶
Mn	13	32.1 * 10 ⁻⁶	44.3 * 10 ⁻⁶	13	26.2 * 10 ⁻⁶	36.1 * 10 ⁻⁶
Ni	38	34.0 * 10 ⁻⁶	46.9 * 10 ⁻⁶	38	12.2 * 10 ⁻⁶	16.9 * 10 ⁻⁶
Zn	6	52.2 * 10 ⁻⁶	72.0 * 10 ⁻⁶	6	79.1 * 10 ⁻⁶	109 * 10 ⁻⁶
U ₃ O ₈ , as U, ⁵	18	44.3 * 10 ⁻⁶	61.1 * 10 ⁻⁶	18	67.1 * 10 ⁻⁶	92.6 * 10 ⁻⁶
H ₂ O	-	0.77	1.06		0.97	1.34
Total amount ⁸	-	3.67	5.06		4.27	5.89

Calculated composition of phosphogypsum from input (mass balance). Values for estimation of water emissions.

¹ Used transfer coefficient from phosphate rock to phosphogypsum.

² Composition values include 0.114 kg CaO from neutralisation of scrubber liquid.

³ Transfer coefficient includes scrubbed fluorine that is not used as co-product H₂SiF₆ product

⁴ Transfer coefficient calculated from average composition of crude phosphoric acid derived from (Ullmann 2001b).

⁵ As emission only considered due to radioactive emissions of the decay products.

63.5.7 Land use

To calculate the land use of the phosphogypsum stacks their lifetime must be known. According to data from Rubin 1995, the lifetime of a stack is usually 10 years. After this time the stack stores 50 Mt phosphogypsum on a typical area of 1.2 km². This leads to a land transformation of 0.0243 m² per ton of phosphogypsum produced or 0.137 m² per ton P₂O₅ (assuming 5.66 kg phosphogypsum produced per kg P₂O₅).

According to data from Becker 1989, for a plant with $1.3 \text{ Mt a}^{-1} \text{ P}_2\text{O}_5$ production the stack area is 1.75 km^2 , the cooling pond area 1.2 km^2 , and the area occupied by the plant infrastructure 0.4 km^2 . Assuming a stack lifetime of 10 years (no further stacks that are already closed) this leads to a land transformation of 0.135 m^2 per ton P_2O_5 for the gypsum stack. The other land occupied is not expanding during the production. For those areas an operating time of 50 years was assumed. This leads to a land transformation of $18.5 * 10^{-3} \text{ m}^2$ per ton P_2O_5 for the cooling pond area and $6.15 * 10^{-3} \text{ m}^2$ per ton P_2O_5 for the plant infrastructure.

The phosphoric acid plants studied in Long & Orne 1990 used 19.7 km^2 for the active storage piles. Additionally, 2.4 km^2 were used for inactive storage piles. In total, there were 600 Mt phosphogypsum stored on the total area (22.1 km^2). This leads to a land transformation of 0.0368 m^2 per ton of gypsum stored. Assumed that 5.66 kg phosphogypsum are produced per kg P_2O_5 in the acid, this leads to a land transformation 0.208 m^2 per ton P_2O_5 for the gypsum stacks. Because most of the stacks are not yet completed, the specific area is higher than the value reported by Rubin 1995. The total area owned by the companies is reported with 87.4 km^2 . A part of this area will be used for future gypsum storage, another part is used for cooling ponds and infrastructure. Further, a considerable part of this area will not be used for direct plant operation and has to be accounted as vegetated industrial area.

With a site map in Nifong 1998, the area not used for gypsum storage (neither for future gypsum storage), cooling ponds, or plant infrastructure was estimated. This area (assumed to be partly vegetated) is two times as large as the cooling pond area. Assuming an occupation time of 50 years of this land, a land transformation of about $37 * 10^{-3} \text{ m}^2$ per ton P_2O_5 was calculated. Within this inventory this type of land was accounted as “industrial area, vegetated”.

For the inventory of the Florida phosphoric acid plant, a transformation to industrial area of $137 * 10^{-6} \text{ m}^2$ per kg P_2O_5 for the stack area was used according to the data of Rubin 1995. For the cooling pond area a transformation to industrial area (built up) of $18.5 * 10^{-6} \text{ m}^2$ per kg P_2O_5 and for the further plant area (without infrastructure) a transformation to industrial area (vegetated) of $37 * 10^{-6} \text{ m}^2$ per kg P_2O_5 was used.

It was assumed that the land before plant operation was pasture and rangeland. After reclamation of the gypsum stacks and cooling ponds the land might be turned back in a kind of “grassland”. According to Thorne 1990, the crust strength and the chemical properties inhibit the natural vegetation on the tailings. With help of amendments it seems possible to re-vegetate the tailings to a green space. For this inventory a land transformation “to pasture and meadow” after reclamation was assumed.

As occupation time for the stack building, 10 years were assumed. Further 50 years of occupation were assumed as reclamation time. This leads to a total occupation as industrial area (built up) of $8.22 * 10^{-3} \text{ m}^2$ a per kg P_2O_5 for the stack area. For the cooling pond area an occupation time of 50 years (plant operation time) and also a reclamation time of 50 years as for the stacks was assumed. This leads to a total occupation as industrial area (built up) of $1.85 * 10^{-3} \text{ m}^2$ a per kg P_2O_5 for the cooling pond area. For the further area (without infrastructure) an occupation time of 50 years (plant operation time) and a reclamation time of 10 years was assumed. This leads to a total occupation as industrial area (vegetated) of $2.22 * 10^{-3} \text{ m}^2$ a per kg P_2O_5 . A summary of the values for the U.S. phosphoric acid production used is given in Tab. 63.10.

The area for the plant infrastructure is not considered here, because this land use (occupation and transformation) belongs to the infrastructure module “phosphoric acid plant”.

For the Moroccan phosphoric acid plants no gypsum stacking and cooling ponds are used. Therefore, no land use (occupation, transformation) was included within the production module. The only land use to consider is the actual area for the plant infrastructure.

Tab. 63.10 Phosphoric acid production. Land use for U.S. (Florida) plant operation.

Land use	Unit	Gypsum storage area		Other area ¹	
		per kg H ₂ PO ₄	per kg P ₂ O ₅	per kg H ₂ PO ₄	per kg P ₂ O ₅
Occupation as industrial area, built up ²	m ² a	5.96 * 10 ⁻⁶	8.22 * 10 ⁻⁶	1.34 * 10 ⁻⁶	1.85 * 10 ⁻⁶
Occupation as industrial area, vegetated ²	m ² a	-	-	1.61 * 10 ⁻⁶	2.22 * 10 ⁻⁶
Transformation from pasture and meadow	m ²	99.3 * 10 ⁻³	137 * 10 ⁻³	40.2 * 10 ⁻³	55.5 * 10 ⁻³
Transformation, to industrial area, built up	m ²	99.3 * 10 ⁻³	137 * 10 ⁻³	13.4 * 10 ⁻³	18.5 * 10 ⁻³
Transformation, to industrial area, vegetation	m ²	-	-	26.8 * 10 ⁻³	37.0 * 10 ⁻³
Transformation, from industrial area, built up	m ²	99.3 * 10 ⁻³	137 * 10 ⁻³	13.4 * 10 ⁻³	18.5 * 10 ⁻³
Transformation, from industrial area, built up	m ²	-	-	26.8 * 10 ⁻³	37.0 * 10 ⁻³
Transformation to pasture and meadow	m ²	99.3 * 10 ⁻³	137 * 10 ⁻³	40.2 * 10 ⁻³	55.5 * 10 ⁻³

For the phosphoric acid production in Morocco no gypsum stacks and cooling ponds are used.

¹ Includes area for cooling ponds and other (vegetated) area connected with the stack and pond system.

² Assumed operating time: 10 years for the gypsum stacks, 50 years for the other areas. Additional 50 years reclamation time for gypsum stacks and cooling ponds. 10 years reclamation time for other (partly vegetated) areas.

63.5.8 Transport processes and infrastructure

The transport of phosphate rock from the mine to the phosphoric acid plant was considered with data from El Hourai et al. 1998 for the Moroccan plant and from Jasinski 2000 and EPA 1994 for the U.S. plants.

The Moroccan rock is transported mainly by rail with an average distance of 150 km to the phosphoric acid plants lying at the shore. One mine operates a conveyor of 100 km to a port. This transport mode was not considered because this mine produces mainly for phosphate rock export and less for acid production. For the Moroccan acid production 3.15 kg phosphate rock per kg P₂O₅ in the acid have to be transported. No transport was assumed for the sulphuric acid because it is produced within the plant areas in Safi or Jorf Lasfar. The transport of the quicklime was neglected. For this inventory 0.473 tkm rail transport were accounted.

For the U.S. phosphate rock the transport mode varies more. Also the distances vary to a larger extend. In Florida a transport distance from the mine to the plant is often 100 km or less. For transport, rail and lorries are used. In some plants also slurry pipes of up to 155 km are used. There was no information available on the exact modal split of those transports. For this inventory 100 km were used as average distance. The transport with slurry pipeline was approximated with rail transport. As modal split 2/3 rail transport and 1/3 road transport was applied. For the U.S. acid production 3.66 kg phosphate rock per kg P₂O₅ in the acid have to be transported. Because the wet rock contains about 10% water (EPA 1994) a weight of 4.02 kg per kg P₂O₅ was used in this inventory. In most cases the phosphoric acid plants operate in the vicinity of a sulphuric acid plant. It was assumed that sulphuric acid has to be transported only in 30% of the cases. For the modal split and the distance, the same assumptions were made as for the phosphate rock. Therefore, additional 3.06 kg sulphuric acid per kg P₂O₅ in the acid have to be transported. Because the acid contains about 5% water, a weight of 3.21 kg per kg P₂O₅ was used in this inventory. The transport of the quicklime was neglected. In this inventory 0.482 tkm rail transport and 0.241 tkm lorry transport were accounted.

For the considered transport operations the modules valid for Europe (location: RER) were applied. The values calculated in tkm are listed in Tab. 63.11.

The infrastructure of the plant, containing the buildings and the equipment, is discussed in Section 63.6. The infrastructure was assessed as plant with an output of $47 \text{ kta}^{-1} \text{ P}_2\text{O}_5$ in the produced phosphoric acid. With this value the infrastructure needed per kg P_2O_5 in the acid was calculated. The Moroccan plant was approximated with the same infrastructure module as used for the U.S. plant.

Tab. 63.11 Phosphoric acid production. Transport processes and infrastructure.

Land use	Unit	Moroccan production		U.S. (Florida) production	
		per kg H_2PO_4	per kg P_2O_5	per kg H_2PO_4	per kg P_2O_5
Phosphoric acid plant ⁴	unit	$3.11 * 10^{-10}$	$4.26 * 10^{-10}$	$3.11 * 10^{-10}$	$4.26 * 10^{-10}$
Transport, lorry, 32t	tkm	-	-	0.175	0.241
Transport, freight, rail	tkm	0.343	0.473	0.349	0.482

¹ Assumed operating time of the plant: 50 years. Infrastructure represent a plant with $47 \text{ kt a}^{-1} \text{ P}_2\text{O}_5$ production.

63.6 Phosphoric acid plant (dihydrate process)

There were no detailed studies on the infrastructure of phosphoric acid plants available. The values for infrastructure were estimated with two reports containing technical data on the process equipment (Felice et al. 1998, Dukhgan & Sadek 1999). The main equipment is the rubber lined reaction tank. The tank size ranges from about 300 m^3 up to 1300 m^3 . In general, 2 m^3 of reaction tank volume are needed per ton of P_2O_5 daily production. New designs work also with half of the reaction volume. For this inventory 2 m^3 per ton of daily P_2O_5 production was used. The amount of material was calculated for a pilot plant in Jordania with a daily production of $150 \text{ t P}_2\text{O}_5$ of acid (Dukhgan & Sadek 1999). There was no data available on the filtering and concentration step. For those steps, the amount of concrete and steel was estimated. For the whole plant about 1400 t (or 636 m^3) concrete, 80 t bricks (protection for reactor lining), 120 t acid resistant steel, 120 t low alloyed steel and 20 t rubber is needed. Further a building is needed which was assumed as building hall (steel) of in total 7000 m^2 area. The rubber lining was approximated with a process for an EPDM rubber. No infrastructure for steam production was included, because the infrastructure of the furnace is already included in the furnace processes (processes: heat, natural gas at industrial furnace 100kW ; heat, heavy fuel oil, at industrial furnace 1 MW ; and heat, at hard coal industrial furnace $1-10\text{MW}$).

For the dismantling of the plant it was assumed that all metal could be recycled. Therefore, no burden for the metals was assumed. The concrete, brick, and rubber were assumed to be land filled. There were no additional emissions considered for a possible contamination of the material. The following processes were used for disposal: "disposal, building, concrete, not reinforced, to final disposal, CH", "disposal, building, brick, to final disposal, CH" and "disposal, polyethylene, 0.4% water, to sanitary landfill".

For the transport of the building materials to the construction site, the standard distances for Europe were used. For brick the same value as for concrete was used (50 km road transport). This leads to a transport demand of $26 * 10^3 \text{ tkm}$ road and $52 * 10^3 \text{ tkm}$ rail for steel and rubber and $74 * 10^3 \text{ tkm}$ road for concrete and brick. For road transport, a 32 t lorry was used.

According to data of Becker 1989, for a plant with $1.3 \text{ Mt a}^{-1} \text{ P}_2\text{O}_5$ production the plant infrastructure occupies 0.4 km^2 . Assuming an operating time of 50 years of the plant, this leads to a land transformation of $6.15 * 10^{-3} \text{ m}^2$ per ton P_2O_5 for the plant infrastructure. For the plant assessed in this infrastructure module, this leads to a plant area of 14460 m^2 . This value was used in this infrastructure module. For the construction and disposal of the plant, further 5 years of occupation as construction site were applied. The occupation of the plant infrastructure site before the use as phosphoric acid plant is not known. Therefore, transformations from unknown were used.

The data in this infrastructure module refer to a plant with an annual phosphoric acid production of $47 \text{ kt P}_2\text{O}_5$ or $65 \text{ kt H}_3\text{PO}_4$ (310 working days per year). With the assumed lifetime of the plant, a pro-

duction amount of 2.33 Mt P₂O₅ or 3.21 Mt H₃PO₄ is achieved during the whole life span. Therefore, 3.11 * 10⁻¹⁰ units per kg H₃PO₄ have to be accounted. A summary of the estimated values is given in Tab. 63.12.

Tab. 63.12 Infrastructure for 47 kt a⁻¹ P₂O₅ phosphoric acid production plant of (crude acid).

Process	Unit	per unit	per kg H ₃ PO ₄ ¹
Concrete, sole plate and foundation, at plant	m ³	636	197 * 10 ⁻⁹
Brick, at plant	kg	80 * 10 ³	24.9 * 10 ⁻⁶
Chromium steel 18/8, at plant	kg	120 * 10 ³	37.3 * 10 ⁻⁶
Steel, low-alloyed, at plant	kg	120 * 10 ³	37.3 * 10 ⁻⁶
Synthetic rubber, at plant	kg	20 * 10 ³	6.2 * 10 ⁻⁶
Building, hall, steel construction	m ²	7 * 10 ³	2.2 * 10 ⁻⁶
Transport, freight, rail	tkm	52 * 10 ³	16.2 * 10 ⁻⁶
Transport, lorry 32t	tkm	100 * 10 ³	31.1 * 10 ⁻⁶
Disposal, building, concrete, not reinforced, to final disposal	kg	1.4 * 10 ⁶	435 * 10 ⁻⁶
Disposal, building, brick, to final disposal	kg	80 * 10 ³	24.9 * 10 ⁻⁶
Disposal, polyethylene, 0.4% water, to sanitary landfill	kg	20 * 10 ³	6.2 * 10 ⁻⁶
Transformation, from unknown	m ²	14.5 * 10 ³	4.58 * 10 ⁻⁶
Transformation, to industrial area, built up	m ²	14.5 * 10 ³	4.58 * 10 ⁻⁶
Occupation, industrial area, built up, ²	m ² a	725 * 10 ³	225 * 10 ⁻⁶
Occupation, construction site, ³	m ² a	72.5 * 10 ³	22.5 * 10 ⁻⁶

¹ Calculated for a product throughput of 65 kt H₃PO₄ per year during the whole lifetime (50 years) of the site. Therefore, 3.11 * 10⁻¹⁰ units of infrastructure are needed per kg phosphoric acid as H₃PO₄.

² Assumed operating time of the plant: 50 years.

³ Time needed for building and removal of the plant after closure: 5 years.

63.7 Allocation of phosphoric acid and fluosilic acid products

Within the production of phosphoric acid from phosphate rock, fluosilic acid is obtained as a co-product. Depending on the economic situation, this acid will be neutralised with quicklime and disposed of or it will be collected and sold on the market. According to data from EFMA 1995, it was assumed that in average an amount of 25 g fluosilic acid (100%) per kg P₂O₅ (or 20 g F per kg P₂O₅) is used as co-product. Calculated per kg H₃PO₄ in the acid, this leads to an amount of 18 g fluosilic acid (100%). As allocation factor the weight of the product (active substance) was used. The used allocation factors are presented in Tab. 63.13.

Tab. 63.13 Allocation of phosphoric acid product and fluosilicic acid co-product from phosphoric acid production.

Process	Unit	Phosphoric acid production, dihydrate process			
		Morocco (MA)		United States (US)	
		per kg H_2PO_4	Allocation Factor, ¹	per kg H_2PO_4	Allocation Factor, ¹
Phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, MA	kg	1	98.2	-	-
Fluosilicic acid, 22% in H ₂ O, at plant, MA	kg	0.018	1.8	-	-
Phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, US	kg	-	-	1	98.2
Fluosilicic acid, 22% in H ₂ O, at plant, US	kg	-	-	0.018	1.8

¹ Allocation according to the mass of the product (active substance) obtained.

63.8 Phosphoric acid, fertiliser grade, GLO; supply mix

63.8.1 Producing countries

North America has a market share of about 30% of the worldwide production of phosphoric acid. The U.S. plants are mainly located in Florida where the bulk load of phosphate rock is mined. An increasing importance has the phosphoric acid production in Morocco. This country has large reserves of phosphate rock and has recently expanded its phosphoric acid capacities. According to El Hourai et al. 1998, the Moroccan phosphoric acid capacity amounts to 3.1 Mt a⁻¹ as P₂O₅, which is more than 50% of the total phosphoric acid capacity operated in Africa (5.8 Mt a⁻¹ as P₂O₅; see Tab. 63.2). Other producing countries of importance are Asia (especially China) and Central Europe and Former Soviet Union.

63.8.2 Assessed supply mix

In this inventory only the production in the United States (Florida) and Morocco was investigated. Thus, the worldwide supply mix presented here is based on these two countries. The production of these two countries makes up about 50% of the worldwide phosphoric acid capacity.

The assessed supply mix for phosphoric acid bases on the phosphoric acid production capacity forecasted by IFA as cited in Maene 1999 for the year 2002. According to this production mix, North America (which is mainly the production in Florida) accounts for 29% of the production and Africa (which is mainly the production in Morocco) accounts for 17%. Calculated on a 100% base this leads to an amount of 63% for U.S. production and 37% for Moroccan production. These numbers (see Tab. 63.14) were applied in order to assess a “worldwide” mix for phosphoric acid production (fertiliser grade). This supply mix is uncertain and incomplete because main phosphoric acid producing countries such as China or Russia were not assessed in this inventory.

Tab. 63.14 Phosphoric acid, fertiliser grade, 70% in H₂O, at plant. Processes used in the global supply mix (GLO).

Production process	Unit	Phosphoric acid, fertiliser grade, 70% in H₂O, at plant, GLO
Phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, US	kg	0.63
Phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, MA	kg	0.37
Total	kg	1.00

¹ Supply mix according to phosphoric acid capacity in North America (US) and Africa (Morocco). Forecasted production capacities for the year 2002 (IFA as cited in Maene 1999).

63.9 Fluosilic acid, 22% in H₂O; supply mix

63.9.1 Introduction

Fluosilicic acid (H₂SiF₆) or hydrofluosilicic acid (Cas.-Nr. 16961-83-4; Mol-weight 144.09 g ml⁻¹) is used mainly in the form of aqueous solutions obtained by the treatment of fluorapatites. Fluosilicic acid is a strong acid in aqueous solution. It has a density of 1.2 kg m⁻³ (at 17.5 °C) as a 22 wt-% solution (Ullmann 2001a)

63.9.2 Production processes

Fluosilicic acid solutions are produced in hydrofluoric acid plants as a result of the presence of silica in the fluorite ore. Approximately 50 kg of H₂SiF₆ is produced per tonne of HF. This represents an annual potential of 50 * 10³ t of fluosilicic acid on a world-wide basis (Ullmann 2001a). Fluosilicic acid is produced during the manufacture of fertilizers or of wet-process phosphoric acid by the action of sulphuric acid on fluorapatite ores. The processes for fluosilicic acid manufacture are normally integrated in the plants for manufacture of superphosphate or phosphoric acid (Ullmann 2001a). Calculated with an amount of 25 g fluosilic acid (100%) per kg P₂O₅, an annual potential of 882 * 10³ t of fluosilicic acid could be produced from phosphoric acid production on a worldwide basis (see Tab. 62.2).

63.9.3 Assessed supply mix

The origin of the fluosilic acid used for the supply mix was not known. According to the calculation above it was assumed that the major part of the fluosilic acid (22wt-% H₂SiF₆) produced originates from the phosphoric acid production. With this assumption, the supply mix was assessed as fluosilic acid production from phosphoric acid production in the United States and in Morocco. Because of the low concentration of the acid, it cannot be assumed that fluosilic acid will be imported from the United States to Europe on a large scale. Because phosphoric acid plants in Europe rather stack the phosphogypsum than releasing it as effluent into the sea (as in Morocco), it also seemed incorrect to apply only the Moroccan production of fluosilic acid.

As an approximation, the same mix as for the worldwide production for phosphoric acid was applied. This mix bases on the phosphoric acid production capacity forecasted by IFA as cited in Maene 1999 for the year 2002. According to this production mix, North America (which is mainly the production in Florida) accounts for 29% of the production and Africa (which is mainly the production in Morocco) accounts for 17%. Calculated on a 100% basis, this leads to an amount of 63% for U.S. production and 37% for Moroccan production. These numbers (see Tab. 63.15) were applied in order to assess an “European” mix for the fluosilic acid production. This supply mix is uncertain and incomplete

because the European fluosilic acid production and fluosilic acid production in hydrofluoric acid plants were not assessed in this inventory.

Tab. 63.15 Fluosilic acid, 22% in H₂O, at plant. Processes used in supply mix for Europe (RER).

Production process	Unit	Fluosilicic acid, 22% in H ₂ O, at plant, RER
Fluosilicic acid, 22% in H ₂ O, at plant, US	kg	0.63
Fluosilicic acid, 22% in H ₂ O, at plant, MA	kg	0.37
Total	kg	1.00

¹ Production mix estimated with the capacity of phosphoric acid in North America (US) and Africa (Morocco). Forecasted production capacities for the year 2002 (IFA as cited in Maene 1999).

63.10 Phosphoric acid industrial grade, 85% in H₂O

63.10.1 Process

The phosphoric acid derived from the wet phosphoric acid process as described, contains many impurities. For industrial use purified acid has often to be used, where the impurities, especially calcium, magnesium aluminium, and iron, but also other inorganic impurities and heavy metals, are removed. For the purification of fertiliser grade phosphoric acid, solvent extraction is the most common process to remove the impurities. In 1990 the production of extractively purified phosphoric acid amounted to 0.3 Mt per year (Ullmann 2001b).

For this inventory only one detailed source for the process was available (Landbank 1994). Further data for the estimation of the composition of process wastes and for process information was derived from Ullmann 2001b and Mc Ketta & Cunningham 1990. A simplified process scheme of phosphoric acid purification is given in Fig. 63.6.

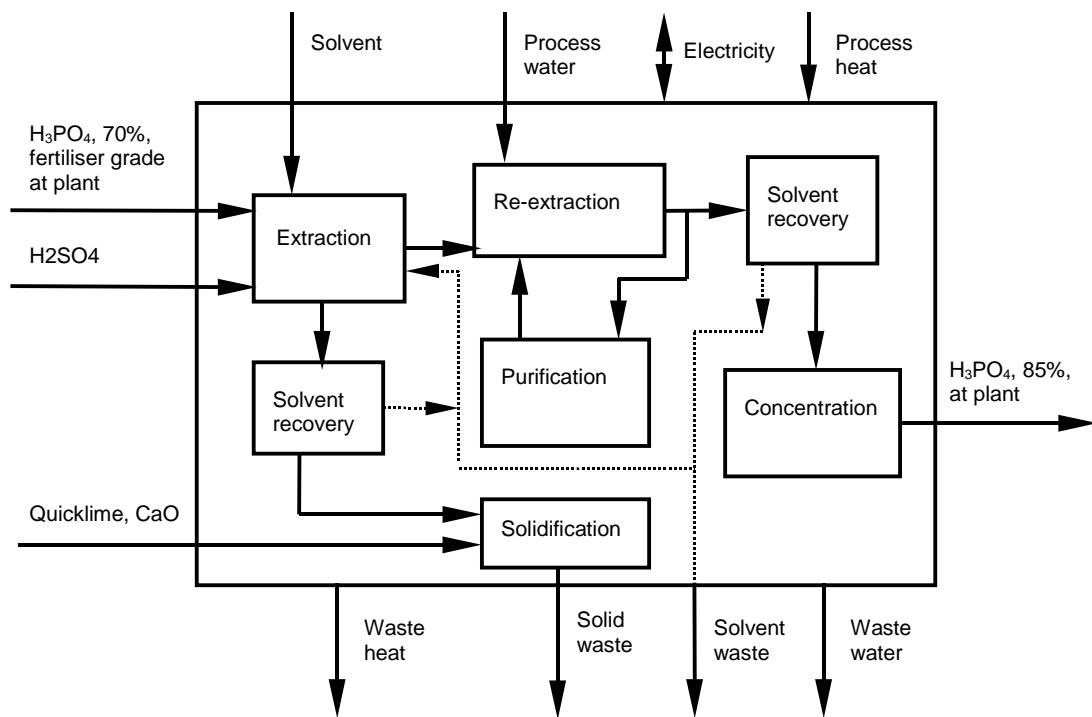


Fig. 63.6 Simplified process of phosphoric acid purification

In this inventory a process with solid process waste according to Landbank 1994 is assumed. Due to the sulphuric acid added during the extraction, a high yield is achieved. According to these data, the yield (in % of P_2O_5 input) is about 98%. A value of 95-98% is given in Ullmann 2001b. The data in this inventory were calculated with a yield of 98% of P_2O_5 input. Other possible production processes, such as so-called splitting processes, were not investigated in this work. In these processes, the yield is much lower (around 50-70%) and the impurities in the aqueous phase are reused in fertiliser production. The extraction process considered produced an extraction raffinate (in addition to the purified acid), which contains all the impurities. This raffinate is reacted with quicklime to obtain a solid waste containing mainly calcium sulphate and hydroxyapatite. In this solid waste, the metals are locked up in the crystal lattice. The obtained waste is land filled (Landbank 1994).

63.10.2 Resources and materials

The resource demands, raw materials and treatment chemicals, were mainly obtained from data of Landbank 1994. The values for the purification step and the solidification of the waste raffinate per kg H_3PO_4 in the purified acid (and per kg P_2O_5) are given in Tab. 63.16. For the process also a solvent is used. There were no data on the solvent type and use included in the data of Landbank 1994. According to Ullmann 2001b, different solvents may be used. It seems likely that isopropanol is one solvent often used in this process. For this inventory it was estimated that 1 kg solvent is needed to process 1 kg P_2O_5 and 1% of the solvent will not be regenerated, but removed as waste. This leads to an estimated amount of 0.01kg isopropanol per kg P_2O_5 in the product acid.

The origin of the phosphoric acid used for purification was not known. An increasing share will origin from countries such as Morocco where phosphate rock mining is expanding. The fertiliser grade phosphoric acid may be produced in a wet-process with stacking of the phosphogypsum (such as in Florida) or it may origin from dry rock production with disposal of the phosphogypsum in the sea. The process assessed in Landbank 1994 uses the latter, but this might not be representative for the whole European production. Due to the lack of information on the distribution, the supply mix for global phosphoric acid production (fertiliser grade, with 70% H_3PO_4) was used in this inventory.

63.10.3 Process energy

According to the data of Landbank 1994, the main energy resource for the process is steam. In the described plant, electricity is produced and the net energy demand of the plant is negative. In Tab. 63.16 the total value is listed, but there are no credits given for electricity production from waste steam within this project. Therefore, it was assumed that the produced energy will be used to a part by the process itself and that the rest is exported without credits (value as in Tab. 63.16).

There was no information available on the energy source for the process steam. It was assumed that the steam would be produced to 50% from heavy fuel oil and to 50% from natural gas.

The data given in Landbank 1994 refer to a product concentration of 56% P in the purified acid. In this inventory a concentration of 61.6% was assessed, so further steam for the concentration step is needed. This further heat demand was calculated from data of Landbank 1994, given for the concentration step of crude phosphoric acid. According to these data, about 2.8 MJ heat is needed per kg of evaporated water. This leads to 0.5MJ per kg P₂O₅ in the product acid additional to the value of 0.529 MJ per kg P₂O₅. The total heat demand is therefore 1.029 MJ per kg P₂O₅. An overview of the values used in this inventory is given in Tab. 63.16.

63.10.4 Emissions and wastes

Besides the solid waste containing the impurities (see above), only emissions to water were reported. The reported amount of emitted sodium fluoride emissions to the water is taken from Landbank 1994. No emissions to air besides water vapour (which is not considered here) was reported and considered. As waste from the solvent replacement, it was assumed that the replaced solvent is incinerated in a hazardous waste incineration plant. For the solid waste it was assumed that it is land filled in a residual material landfill.

63.10.5 Transport and infrastructure

For the transport of the impure (fertiliser grade) acid it was assumed that the production of the impure acid occurs in vicinity of the phosphate ores and, due to environmental and economic reasons, generally not in Europe. Transport of the acid to the purification plant was considered. There was no further information on the distances available. The distances were estimated referring to the case described in Landbank 1994, where the production is in Morocco and the purification takes place in England. The following distances for the fertiliser grade acid (70% P₂O₅) were included: 2000 km overseas transport, 200 km rail transport, and 100 km road transport. For the other chemicals, with exception of the lime, the standard distances for Europe of 600 km rail transport and 100 km road transport were applied. For quicklime distances of 100 km rail and 100 km road were used. For the disposal of the solid waste, 50km road transport were assumed. It was assumed that the solvent incineration occurs on the plant site.

No information was available on the infrastructure needs of the plant. It was assumed that the importance of infrastructure is low and the consumption of materials would be similar to plants producing organic chemicals. Therefore, the module “chemical plant, organics” was used. For this module with a production capacity of 50'000 t per year and a plant lifetime of 50 years, an amount of $4 * 10^{-10}$ units per kg product acid or $6.5 * 10^{-10}$ units per kg P₂PO₅ in the product acid was assumed. Since the product acid contains 85% H₂PO₄, this corresponds to $4.7 * 10^{-10}$ per kg H₂PO₄ (see table below).

Tab. 63.16 Phosphoric acid purification. Values used for the inventory.

Land use	Unit	Acid purification, RER		Remarks
		per kg H ₂ PO ₄	per kg P ₂ O ₅	
Phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant; ¹	kg	1.020	1.41	as H ₃ PO ₄ , global production mix used.
Sulphuric acid, liquid, at plant	kg	0.129	0.179	(Landbank 1994),
Sodium hydroxide, 50% in H ₂ O, at plant	kg	0.026	0.036	(Landbank 1994),
Quicklime, milled, loose, at plant	kg	0.108	0.149	(Landbank 1994),
Isopropanol, at plant	kg	0.007	0.01	Estimation
Electricity; ²	kWh	-0.042	-0.058	Total value in /out
Heat, natural gas, at industrial furnace >100kW; ³	MJ	0.372	0.514	Of total 1.029 MJ heat 0.5 MJ refers to a concentration step from 75% H ₃ PO ₄ to 85% H ₃ PO ₄ .
Heat, heavy fuel oil, at industrial furnace 1MW; ³	MJ	0.372	0.514	
Water, deionised, at plant	kg	1.09	1.51	for steam
Water, well, in ground	m ³	5.0 * 10 ⁻⁴	6.9 * 10 ⁻⁴	for processing
Sodium, ion, to water	kg	0.0017	0.0023	0.031 kg NaF / kg H ₃ PO ₄ ; (Landbank 1994),
Fluoride	kg	0.0014	0.0019	
Disposal, solvents mixture, 0% water, to hazardous waste incineration	kg	0.007	0.01	
Disposal, H ₃ PO ₄ purification residue, 0% water, to residual material landfill	kg	0.352	0.486	(Landbank 1994),
Transport, lorry, 32t	tkm	0.20	0.27	
Transport, freight, rail	tkm	0.47	0.65	
Transport, transoceanic tanker	tkm	3.31	4.57	
Chemical plant, organics	tkm	4.7 * 10 ⁻¹⁰	6.5 * 10 ⁻¹⁰	Approximation

¹ Assumed yield on P₂O₅ : 98%; transport to plant assumed with 100 km road, 200 km rail and 2000 km sea.

² Electricity of 0.15 kWh per kg P₂O₅ is produced at site. No credit for this electricity production was given. The negative value stated was neglected and the electricity demand was considered with 0 kWh.

³ Assumed split for the heat production: 50% natural gas, 50% fuel oil.

63.10.6 Waste composition

The solid waste produced in this process contains the impurities of the fertiliser grade acid. In order to calculate the emissions within the waste process, the composition of this solid waste was calculated. As reference for the amount of impurities in the processed acid, the concentrations for a typical crude phosphoric acid given in Ullmann 2001b were used. Missing values for cadmium and mercury were estimated using data from Becker 1989 for the phosphate rock and calculated with a transfer coefficient of 80% to the acid and 20% to the phosphogypsum (Ullmann 2001b). According to Landbank 1994, 1.986 kg crude acid are needed to produce 1 kg of pure phosphoric acid with a concentration of 56% P₂O₅. In the concentration step of the crude acid to a commercial concentration of about 55% P, fluoride emission are released which have to be subtracted from the amount of impurities. According to Landbank 1994, 28 g fluoride emissions are released in this step per 1 kg of pure phosphoric acid with a concentration of 56% P₂O₅. In addition to the impurities, the chemicals used in the purification step, such as H₂SO₄, NaOH, CaO, have to be considered as further inputs to the waste stream. The values stated in Tab. 63.16 were used in the calculations. For phosphorus, a P₂O₅ efficiency of the purification process of 98% was assumed.

According to Landbank 1994, an amount of solid waste of 0.272 kg is produced per 1 kg of pure phosphoric acid with a concentration of 56% P₂O₅. This waste contains about 83% calcium sulphate [CaSO₄] and 8.3% hydroxy apatite [Ca₁₀(PO₄)₆(OH)₂] The elemental composition of the waste is given in Tab. 63.17.

Tab. 63.17 Phosphoric acid purification waste. Elemental composition.

Element	Unit	Amount per kg waste	Remarks
P	kg	1.53E-02	
Ca	kg	2.74E-01	
F	kg	4.82E-02	
Si	kg	2.86E-02	
S	kg	1.93E-01	
Mg	kg	9.08E-03	
Fe	kg	5.59E-03	
Al	kg	2.80E-03	
Cr	kg	1.54E-03	
Zn	kg	1.33E-03	
V	kg	9.08E-04	
Ni	kg	2.38E-04	
Cu	kg	1.89E-04	
Mn	kg	6.30E-05	
As	kg	4.89E-05	
Pb	kg	1.40E-05	
Cd	kg	7.10E-05	
Hg	kg	4.74E-07	
O	kg	4.19E-01	without O ₂ in Water
H ₂ O	kg	0.00E+00	Water content

63.11 Data quality considerations

Tab. 63.18 and Tab. 63.19 show the data quality indicators for the inventory of wet phosphoric acid production in the U.S. (Florida). Tab. 63.20 presents the data quality indicators for the inventory of wet phosphoric acid production in Morocco. The allocation of the inputs to the two products, phosphoric acid and fluosilic acid, is also presented in these tables. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation, and sample size. Good data was available on the resources used. Also the data for the energy demand seem reliable. On the contrary, the amount of energy derived from steam of sulphuric acid plants is uncertain. This steam bears no burden within the methodology of this project. The used amount could have an important effect on the result, because it replaces fossil fuels within the phosphoric acid plant. There were only little and very general data available on the energy split of the used steam. Thus, the uncertainty of the used energy processes may nevertheless be considerable.

A high uncertainty exists for the amount of short-term emissions to water within the U.S. phosphoric acid production. Also emissions to air have a high uncertainty because of the lack of specific data of the plants, which made a distinction between the production processes not possible. Overall, the data presented for the Moroccan acid production are more uncertain because data of the Moroccan production was scarce and therefore data of U.S. producers was often used to assess the Moroccan production processes. In general, the infrastructure data (presented in Tab. 63.19) has a high uncertainty because only few data was available for the assessment.

The highest uncertainty comes along with the amount of long-term emissions to water and air. Since the uncertainty is too high to have reliable estimations, the long-term emissions presented in Tab. 63.18 and Tab. 63.19 were not included in the ecoinvent database.

Within the derived product and co-product (fluosilic acid), there is large uncertainty on the amount of fluosilic acid effectively produced. There were only very general statements on the production split available. Therefore, also the allocation made contains further uncertainty. The assessed production mixes (phosphoric acid, GLO; fluosilic acid, RER) are uncertain, because the production was assessed only for two major producing countries, which cover about 50% of the worldwide phosphoric acid capacity. Other large producers such as China and Russia were not considered in this inventory. Therefore, this mix contains a high uncertainty.

The process for purification of phosphoric acid bases only on data of one producer in the United Kingdom and may therefore not be representative for the whole area assessed (RER). The data used seems reliable but there are possibly some emissions or wastes missing. The infrastructure for this module was approximated with an average chemical plant site and is therefore highly uncertain. The in- output data for the purified industrial grade phosphoric acid is presented in Tab. 62.14.

Tab. 63.18 In- / outputs for the module “phosphoric acid production, dihydrate process” and the allocated products “phosphoric fertiliser grade” and “fluosilic acid”, location US

Process output of multi output process: phosphoric acid production, dihydrate process, US						Allocated product outputs per 1 kg Product		
	Name, Location	Value	Unit	Uncertainty	Comment	phosphoric acid, fertiliser grade, 70% H ₂ O, at plant, US	fluosilic acid, 22% in H ₂ O, at plant, US	
From technosphere	phosphate rock, as P2O5, beneficiated, wet, at plant, US	7.68E-1	kg	lognorm	1,3,3,1,1,3	1.14 Data for wet rock process, assumptions	7.54E-1	7.68E-1
	phosphoric acid plant, fertiliser grade, US	3.11E-10	unit	lognorm	4,5,1,5,4,5	3.38 Data from a small plant in Jordania	3.05E-10	3.11E-10
	sulphuric acid, liquid, at plant, RER	2.22E+0	kg	lognorm	2,4,4,3,3,5	1.40 Data for a specific wet rock process, assumptions	2.18E+0	2.22E+0
	quicklime, milled, loose, at plant, CH	8.26E-2	kg	lognorm	2,3,3,5,3,5	1.35 Data for an average process from literature	8.11E-2	8.26E-2
	electricity, medium voltage, production UCTE, at grid, UC	1.38E-1	kW h	lognorm	2,1,1,5,1,3	1.14 Average value for U.S. production used	1.36E-1	1.38E-1
	heat, natural gas, at industrial furnace >100kW, RER	3.06E+0	MJ	lognorm	3,2,2,3,3,4	1.27 Average of different literature, split is uncertain	3.00E+0	3.06E+0
	heat, heavy fuel oil, at industrial furnace 1MW, CH	1.20E-1	MJ	lognorm	3,2,2,3,3,4	1.27 Average of different literature, split is uncertain	1.18E-1	1.20E-1
	heat, at hard coal industrial furnace 1-10MW, RER	4.00E-1	MJ	lognorm	3,2,2,3,3,4	1.27 Average of different literature, split is uncertain	3.93E-1	4.00E-1
	transport, lorry 32t, RER	1.75E-1	tkm	lognorm	3,4,1,3,1,5	2.07 From plant location obtained, split uncertain	1.72E-1	1.75E-1
	transport, freight, rail, RER	3.49E-1	tkm	lognorm	3,4,1,3,3,5	2.12 From plant location obtained, split uncertain	3.43E-1	3.49E-1
Resources	(Water, well, in ground	2.63E-3	m3	lognorm	2,3,4,1,3,4	1.33 Data for a specific wet rock process, assumptions	2.58E-3	2.63E-3
	Occupation, industrial area, built up	7.30E-6	m2a	lognorm	2,2,3,1,1,4	1.54 Data for a different sources, assumptions	7.17E-6	7.30E-6
	Occupation, industrial area, vegetation	1.61E-6	m2a	lognorm	2,2,3,1,1,4	2.03 Data for a different sources, assumptions	1.58E-6	1.61E-6
	Transformation, from pasture and meadow	1.40E-1	m2	lognorm	2,2,3,1,1,4	2.03 Data for a different sources, assumptions	1.37E-1	1.40E-1
	Transformation, to industrial area, built up	1.13E+2	m2	lognorm	2,2,3,1,1,4	2.03 Data for a different sources, assumptions	1.11E+2	1.13E+2
	Transformation, industrial area, vegetation	2.68E-2	m2	lognorm	2,2,3,1,1,4	2.03 Data for a different sources, assumptions	2.63E-2	2.68E-2
	Transformation, from industrial area, built up	1.13E+2	m2	lognorm	2,2,3,1,1,4	2.03 Data for a different sources, assumptions	1.11E+2	1.13E+2
	Transformation, from industrial area, vegetation	2.68E-2	m2	lognorm	2,2,3,1,1,4	2.03 Data for a different sources, assumptions	2.63E-2	2.68E-2
	Transformation, to pasture and meadow	1.40E-1	m2	lognorm	2,2,3,1,1,4	2.03 Data for a different sources, assumptions	1.37E-1	1.40E-1
	Heat, waste, air, low population density	4.98E-1	MJ	lognorm	2,1,1,5,1,3	1.14 Calculated from electricity use	4.89E-1	4.98E-1
Emissions to air	Hydrogen fluoride, air, low population density	5.29E-5	kg	lognorm	2,5,2,5,5,5	2.77 large variation possible, average value used	5.19E-5	5.29E-5
	Hydrogen fluoride, air, low population density, long-term	2.90E-4	kg	lognorm	4,5,1,1,5,5	2.80 Estimated from weak data, assumptions	2.85E-4	2.90E-4
	Silicon tetrafluoride, air, low population density	3.60E-6	kg	lognorm	4,5,1,1,5,5	2.80 Estimated from weak data, assumptions	3.54E-6	3.60E-6
	Silicon tetrafluoride, air, low population density, long-term	3.60E-4	kg	lognorm	4,5,1,1,5,5	2.80 Estimated from weak data, assumptions	3.54E-4	3.60E-4
	Particulates, > 10 µm, air, low population density	1.50E-4	kg	lognorm	2,5,4,1,4,5	1.93 Related process data used, uncertain distribution	1.47E-4	1.50E-4
	Particulates, > 2.5 µm, and < 10µm, air, low population density	1.70E-4	kg	lognorm	2,5,4,1,4,5	2.37 Related process data used, uncertain distribution	1.67E-4	1.70E-4
	Particulates, < 2.5 µm, air, low population density	1.20E-4	kg	lognorm	2,5,4,1,4,5	3.37 Related process data used, uncertain distribution	1.18E-4	1.20E-4
	Uranium-238, air, low population density	2.46E-5	kgBa	lognorm	3,4,1,2,5,5	3.74 Data from one survey, distribution uncertain	2.42E-5	2.46E-5
	Thorium-228, air, low population density	7.04E-6	kgBa	lognorm	3,4,1,2,5,5	3.74 Data from one survey, distribution uncertain	6.91E-6	7.04E-6
	Radium-226, air, low population density	3.17E-4	kgBa	lognorm	3,4,1,2,5,5	3.74 Data from one survey, distribution uncertain	3.11E-4	3.17E-4
1)	Radon-222, air, low population density	2.89E+0	kgBa	lognorm	3,4,1,2,5,5	3.74 Data from one survey, distribution uncertain	2.84E+0	2.89E+0
	Lead-210, air, low population density	2.82E-4	kgBa	lognorm	3,4,1,2,5,5	3.74 Data from one survey, distribution uncertain	2.77E-4	2.82E-4
	Polonium-210, air, low population density	4.93E-4	kgBa	lognorm	3,4,1,2,5,5	3.74 Data from one survey, distribution uncertain	4.84E-4	4.93E-4
	Potassium-40, air, low population density	2.82E-5	kgBa	lognorm	3,4,1,2,5,5	3.74 Data from one survey, distribution uncertain	2.77E-5	2.82E-5
1)	phosphoric acid, fertiliser grade, 70% H ₂ O, at plant, US	1.00E+0	kg	-	- not applicable	- Uncertainty not applicable for allocated product	-	-
	fluosilic acid, 22% in H ₂ O, at plant, US	1.80E-2	kg	-	- not applicable	- Uncertainty not applicable for allocated product	-	-
(1) Allocated products							Applied allocation factor :	98.2% 1.8%

Tab. 62.18 (Continuation) In- / outputs for the module “phosphoric acid production, dihydrate process” and the allocated products “phosphoric fertiliser grade” and “fluosilicic acid”, location US

Process output of multi output process: phosphoric acid production, dihydrate process, US						Allocated product outputs per 1 kg Product
Name, Location	Value	Unit	Uncertainty	Comment	phosphoric acid, fertiliser grade, 70% H ₂ O, at plant, US	fluosilicic acid, 22% in H ₂ O, at plant, US
		Type	Score	St.Dev.		
Fluoride, water, ground-	2.10E-7	kg	lognorm	4,5,1,1,4,5	1.92	Estimation based on 1 Source, calculated
Fluoride, water, ground-, long-term	4.20E-4	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Values calculated
Calcium, ion, water, ground-	4.70E-5	kg	lognorm	3,4,1,1,1,5	1.59	Estimation based on 1 Source, calculated
Calcium, ion, water, ground-, long-term	9.40E-2	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Sulfate, water, ground-	1.06E-4	kg	lognorm	3,4,1,1,1,5	1.59	Estimation based on 1 Source, calculated
Sulfate, water, ground-, long-term	2.11E-1	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Phosphate, water, ground-	2.91E-6	kg	lognorm	3,4,1,1,1,5	1.59	Estimation based on 1 Source, calculated
Phosphate, water, ground-, long-term	5.82E-3	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Cadmium, ion, water, ground-	1.54E-9	kg	lognorm	3,4,1,1,1,5	5.08	Estimation based on 1 Source, calculated
Cadmium, ion, water, ground-, long-term	3.08E-6	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Lead, water, ground-	1.50E-10	kg	lognorm	3,4,1,1,1,5	5.08	Estimation based on 1 Source, calculated
Lead, water, ground-, long-term	3.00E-7	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Arsenic, ion, water, ground-	7.40E-10	kg	lognorm	3,4,1,1,1,5	5.08	Estimation based on 1 Source, calculated
Arsenic, ion, water, ground-, long-term	1.48E-6	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Chromium, ion, water, ground-	9.50E-11	kg	lognorm	3,4,1,1,1,5	5.08	Estimation based on 1 Source, calculated
Chromium, ion, water, ground-, long-term	1.90E-7	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Copper, ion, water, ground-	3.64E-9	kg	lognorm	3,4,1,1,1,5	5.08	Estimation based on 1 Source, calculated
Copper, ion, water, ground-, long-term	7.27E-6	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Manganese, water, ground-	1.31E-9	kg	lognorm	3,4,1,1,1,5	5.08	Estimation based on 1 Source, calculated
Manganese, water, ground-, long-term	2.62E-6	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Nickel, ion, water, ground-	6.10E-10	kg	lognorm	3,4,1,1,1,5	5.08	Estimation based on 1 Source, calculated
Nickel, ion, water, ground-, long-term	1.22E-6	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Zinc, ion, water, ground-	3.96E-9	kg	lognorm	3,4,1,1,1,5	5.08	Estimation based on 1 Source, calculated
Zinc, ion, water, ground-, long-term	7.91E-6	kg	lognorm	not applicable	10.00	Estimated 1-100% Emission, Value calculated
Uranium-238, water, ground-	5.90E-4	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Uranium-238, water, ground-, long-term	1.18E+0	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Thorium-228, water, ground-	1.41E-5	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Thorium-228, water, ground-, long-term	2.82E-2	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Radium-226, water, ground-	1.30E-3	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Radium-226, water, ground-, long-term	2.59E+0	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Lead-210, water, ground-	1.15E-3	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Lead-210, water, ground-, long-term	2.30E+0	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Polonium-210, water, ground-	1.76E-3	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Polonium-210, water, ground-, long-term	3.51E+0	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Potassium-40, water, ground-	1.39E-4	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
Potassium-40, water, ground-, long-term	2.78E-1	kBq	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain
) phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, US	1.00E+0	kg	- not applicable	-	- Uncertainty not applicable for allocated product	-
) fluosilicic acid, 22% in H ₂ O, at plant, US	1.80E-2	kg	- not applicable	-	- Uncertainty not applicable for allocated product	-
1) Allocated products					Applied allocation factor :	98.2% 1.8%

Tab. 63.19 In- / outputs for the module “phosphoric acid plant, fertiliser grade”, location US

Process output: 1 unit, phosphoric acid plant, fertiliser grade, US						
Name, Location	Value	Unit	Uncertainty	Comment		
		Type	Score	St.Dev.		
synthetic rubber, at plant, RER	2.00E+4	kg	lognorm	4,5,1,5,4,5	1.69	Estimated with data from a small Jordanian plant
chromium steel 18/8, at plant, RER	1.20E+5	kg	lognorm	4,5,1,5,4,5	1.69	Estimated with data from a small Jordanian plant
steel, low-alloyed, at plant, RER	1.20E+5	kg	lognorm	4,5,1,5,4,5	1.69	Estimated with data from a small Jordanian plant
concrete, sole plate and foundation, at plant, CH	6.36E+2	m3	lognorm	4,5,1,5,4,5	1.69	Estimated with data from a small Jordanian plant
brick, at plant, RER	8.00E+4	kg	lognorm	4,5,1,5,4,5	1.69	Estimated with data from a small Jordanian plant
building, hall, steel construction, CH	7.00E+3	m2	lognorm	4,5,1,5,4,5	3.38	Estimated with data from a small Jordanian plant
disposal, polyethylene, 0.4% water, to sanitary landfill, CH	2.01E+4	kg	lognorm	4,5,1,5,4,5	1.69	Estimated with data from a small Jordanian plant
disposal, building, concrete, not reinforced, to final disposal,	1.40E+6	kg	lognorm	4,5,1,5,4,5	1.69	Estimated with data from a small Jordanian plant
disposal, building, brick, to final disposal, CH	8.00E+4	kg	lognorm	4,5,1,5,4,5	1.69	Estimated with data from a small Jordanian plant
transport, lorry 32t, RER	1.00E+5	tkm	lognorm	4,5,nA,5,nA,nA	2.11	Estimated with standard distances for europe
transport, freight, rail, RER	5.20E+4	tkm	lognorm	4,5,nA,5,nA,nA	2.11	Estimated with standard distances for europe
Occupation, construction site	7.25E+4	m2a	lognorm	3,4,4,1,3,5	1.70	Estimated with data from one large plant in Florida
Occupation, industrial area, built up	7.25E+5	m2a	lognorm	3,4,4,1,3,5	1.70	Estimated with data from one large plant in Florida
Transformation, from unknown	1.45E+4	m2	lognorm	3,4,4,1,3,5	2.17	Estimated with data from one large plant in Florida
⇒ Transformation, to industrial area, built up	1.45E+4	m2	lognorm	3,4,4,1,3,5	2.17	Estimated with data from one large plant in Florida
1) Ressources						

Tab. 63.20 In- / outputs for the module “phosphoric acid production, dihydrate process” and the allocated products “phosphoric fertiliser grade” and “fluosilic acid”, location MA

Process output of multi output process: phosphoric acid production, dihydrate process, MA							Allocated product outputs per 1 kg product		
	Name, Location	Value	Unit	Uncertainty		Comment	phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, MA	fluosilic acid, 22% in H ₂ O, at plant, MA	
				Type	Score	St.Dev.			
from technosphere	phosphate rock, as P ₂ O ₅ , beneficiated, dry, at plant, MA	7.53E-1	kg	lognorm	1,3,2,1,1,3	1.09	Data for dry rock process, assumptions	7.39E-1	7.53E-1
	phosphoric acid plant, fertiliser grade, US	3.11E-10	unit	lognorm	4,5,1,5,4,5	3.38	Data from a small plant in Jordania	3.05E-10	3.11E-10
	sulphuric acid, liquid, at plant, RER	1.84E+0	kg	lognorm	2,4,4,5,3,5	1.42	Data for a specific dry rock process, assumptions	1.81E+0	1.84E+0
	quicklime, milled, loose, at plant, CH	8.26E-2	kg	lognorm	2,3,3,5,3,5	1.35	Data for an average process from literature	8.11E-2	8.26E-2
	electricity, medium voltage, production UCTE, at grid, UCTE	1.38E-1	kWh	lognorm	2,1,1,5,4,3	1.53	Average value for U.S. production used	1.36E-1	1.38E-1
	heat, natural gas, at industrial furnace >100kW, RER	3.06E+0	MJ	lognorm	3,2,2,5,3,4	1.29	Average of different literature, split is uncertain	3.00E+0	3.06E+0
	heat, heavy fuel oil, at industrial furnace 1MW, CH	1.20E-1	MJ	lognorm	3,2,2,5,3,4	1.29	Average of different literature, split is uncertain	1.18E-1	1.20E-1
	heat, at hard coal industrial furnace 1-10MW, RER	4.00E-1	MJ	lognorm	3,2,2,5,3,4	1.29	Average of different literature, split is uncertain	3.93E-1	4.00E-1
	transport, freight, rail, RER	3.43E-1	tkm	lognorm	3,3,1,1,3,5	2.11		3.37E-1	3.43E-1
1)	Water, cooling, unspecified natural origin	5.14E-2	m ³	lognorm	2,3,2,1,3,4	1.25	Data from one relevant source used	5.05E-2	5.14E-2
	Water, well, in ground	3.71E-3	m ³	lognorm	2,3,2,1,3,4	1.25	Data from one relevant source used	3.64E-3	3.71E-3
Emissions to air	Heat, waste, air, low population density	4.98E-1	MJ	lognorm	2,1,1,5,1,3	1.14	Calculated from electricity use	4.89E-1	4.98E-1
	Carbon dioxide, fossil, air, low population density	1.25E-1	kg	lognorm	3,3,4,1,3,5	1.40	Data for dry rock processing, one source	1.23E-1	1.25E-1
	Hydrogen fluoride, air, low population density	5.00E-5	kg	lognorm	2,5,2,5,5,5	2.77	large variation possible, average value used	4.91E-5	5.00E-5
	Particulates, > 10 µm, air, low population density	1.50E-4	kg	lognorm	2,5,4,5,4,5	1.94	Related process data used, uncertain distribution	1.47E-4	1.50E-4
	Particulates, > 2.5 µm, and < 10µm, air, low population density	1.70E-4	kg	lognorm	2,5,4,5,4,5	2.39	Related process data used, uncertain distribution	1.67E-4	1.70E-4
	Particulates, < 2.5 µm, air, low population density	1.20E-4	kg	lognorm	2,5,4,5,4,5	3.38	Related process data used, uncertain distribution	1.18E-4	1.20E-4
	Uranium-238, air, low population density	2.46E-5	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	2.42E-5	2.46E-5
	Thorium-228, air, low population density	7.04E-6	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	6.91E-6	7.04E-6
	Radium-226, air, low population density	3.17E-4	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	3.11E-4	3.17E-4
	Radon-222, air, low population density	2.89E+0	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	2.84E+0	2.89E+0
	Lead-210, air, low population density	2.82E-4	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	2.77E-4	2.82E-4
	Polonium-210, air, low population density	4.93E-4	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	4.84E-4	4.93E-4
	Potassium-40, air, low population density	2.82E-5	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	2.77E-5	2.82E-5
Emissions to water	Fluoride, water, ocean	9.10E-3	kg	lognorm	3,4,4,1,1,5	1.65	Calculated from composition of phosphate rock	8.94E-3	9.10E-3
	Calcium, ion, water, ocean	8.83E-1	kg	lognorm	3,4,4,1,1,5	1.65	Calculated from composition of phosphate rock	8.67E-1	8.83E-1
	Sulfate, water, ocean	1.75E+0	kg	lognorm	3,4,4,1,1,5	1.65	Calculated from composition of phosphate rock	1.72E+0	1.75E+0
	Phosphate, water, ocean	3.88E-2	kg	lognorm	3,4,4,1,1,5	1.65	Calculated from composition of phosphate rock	3.81E-2	3.88E-2
	Cadmium, ion, water, ocean	1.90E-5	kg	lognorm	3,4,4,1,1,5	5.13	Calculated from composition of phosphate rock	1.87E-5	1.90E-5
	Lead, water, ocean	2.60E-6	kg	lognorm	3,4,4,1,1,5	5.13	Calculated from composition of phosphate rock	2.55E-6	2.60E-6
	Arsenic, ion, water, ocean	5.02E-5	kg	lognorm	3,4,4,1,1,5	5.13	Calculated from composition of phosphate rock	4.93E-5	5.02E-5
	Chromium, ion, water, ocean	5.60E-6	kg	lognorm	3,4,4,1,1,5	5.13	Calculated from composition of phosphate rock	5.50E-6	5.60E-6
	Copper, ion, water, ocean	6.20E-6	kg	lognorm	3,4,4,1,1,5	5.13	Calculated from composition of phosphate rock	6.09E-6	6.20E-6
	Manganese, water, ocean	3.21E-5	kg	lognorm	3,4,4,1,1,5	5.13	Calculated from composition of phosphate rock	3.15E-5	3.21E-5
	Nickel, ion, water, ocean	3.40E-5	kg	lognorm	3,4,4,1,1,5	5.13	Calculated from composition of phosphate rock	3.34E-5	3.40E-5
	Zinc, ion, water, ocean	5.22E-5	kg	lognorm	3,4,4,1,1,5	5.13	Calculated from composition of phosphate rock	5.13E-5	5.22E-5
	Uranium-238, water, ocean	1.18E+0	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	1.16E+0	1.18E+0
	Thorium-228, water, ocean	2.82E-2	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	2.77E-2	2.82E-2
	Radium-226, water, ocean	2.59E+0	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	2.54E+0	2.59E+0
	Lead-210, water, ocean	2.30E+0	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	2.26E+0	2.30E+0
	Polonium-210, water, ocean	3.51E+0	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	3.45E+0	3.51E+0
	Potassium-40, water, ocean	2.78E-1	kg ⁰	lognorm	3,4,1,2,5,5	3.74	Data from one survey, distribution uncertain	2.73E-1	2.78E-1
2)	phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, MA	1.00E+0	kg	-	not applicable	-	Uncertainty not applicable for allocated product	-	-
	fluosilic acid, 22% in H ₂ O, at plant, MA	1.80E-2	kg	-	not applicable	-	Uncertainty not applicable for allocated product	-	-
1) Ressources; 2) Allocated products							Applied allocation factor :	98.2%	1.8%

Tab. 63.21 In- / outputs for the supply mix “phosphoric acid, fertiliser grade, at plant”, location GLO

Process output: 1 kg, phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, GLO						
Name, Location	Value	Unit	Uncertainty		Comment	
			Type	Score	St.Dev.	
phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, US	6.30E-1	kg	lognorm	1,3,1,3,3,3	1.22	About 10% of the world production included
phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, MA	3.40E-1	kg	lognorm	1,3,1,3,3,3	1.22	About 10% of the world production included

Tab. 63.22 In- / outputs for the supply mix “fluosilic acid, 22% in H₂O, at plant”, location RER

Process output: 1 kg, fluosilic acid, 22% in H ₂ O, at plant, RER						
Name, Location	Value	Unit	Uncertainty		Comment	
			Type	Score	St.Dev.	
fluosilic acid, 22% in H ₂ O, at plant, US	6.30E-1	kg	lognorm	5,5,1,5,3,5	1.69	Approximation, no information on distribution
fluosilic acid, 22% in H ₂ O, at plant, MA	3.40E-1	kg	lognorm	5,5,1,5,3,5	1.69	Approximation, no information on distribution

Tab. 63.23 In- / outputs for the module “phosphoric acid, industrial grade, 85% in H₂O, at plant”, location RER

Process output: 1 kg, phosphoric acid, industrial grade, 85% in H ₂ O, at plant, RER					
Name, Location	Value	Unit	Type	Score	St.Dev.
from technosphere	phosphoric acid, fertiliser grade, 70% in H ₂ O, at plant, GLO	1.02E+0	kg	lognorm	2,4,2,1,1,5
	sodium hydroxide, 50% in H ₂ O, production mix, at plant, RE	2.60E-2	kg	lognorm	2,4,2,1,1,5
	chemical plant, organics, RER	4.70E-10	unit	lognorm	5,5,1,1,5,5
	sulphuric acid, liquid, at plant, RER	1.29E-1	kg	lognorm	2,4,2,1,1,5
	quicklime, milled, loose, at plant, CH	1.08E-1	kg	lognorm	2,4,2,1,1,5
	isopropanol, at plant, RER	7.00E-3	kg	lognorm	5,5,1,1,5,5
	water, deionised, at plant, CH	1.09E+0	kg	lognorm	2,4,2,1,1,5
	heat, natural gas, at industrial furnace >100kW, RER	3.72E-1	MJ	lognorm	4,4,2,1,3,5
	heat, heavy fuel oil, at industrial furnace 1MW, CH	3.72E-1	MJ	lognorm	4,4,2,1,3,5
	disposal, H ₃ PO ₄ purification residue, 0% water, to residual r	3.52E-1	kg	lognorm	2,4,2,1,1,5
	disposal, solvents mixture, 16.5% water, to hazardous waste	7.00E-3	kg	lognorm	5,5,1,1,5,5
	transport, lorry 32t, RER	2.00E-1	tkm	lognorm	4,5,1,1,3,5
	transport, freight, rail, RER	4.70E-1	tkm	lognorm	4,5,1,1,3,5
	transport, transoceanic tanker, OCE	3.31E+0	tkm	lognorm	4,5,1,1,3,5
↪ Water, well, in ground,	5.00E-4	m ³	lognorm	2,4,2,1,1,5	1.24
↪ Sodium, ion, water, unspecified	1.70E-3	kg	lognorm	2,4,2,1,1,5	1.58
↪ Fluoride, water, unspecified	1.40E-3	kg	lognorm	2,4,2,1,1,5	1.58

(1) Ressources; 2) Emissions to water

63.12 Cumulative results and interpretation

Results of the cumulative inventory of both datasets can be downloaded from the database.

63.13 Conclusions

The production of phosphate rock has a large variety due to different ore grades (small or large oversize) and beneficiation processes (dry, wet). Therefore, the assessment process has to deal with various uncertainties of the data. For the water use and also for possible emissions to water the climate and soil structure may need further attention in future works. There was a lack of reliable data especially for particle emissions of rock handling and storage, which seems to be an important emission source. Also most data concern U.S. production and only few data for Moroccan phosphate rock was available. In order to assess a representative average for world-wide phosphate mining also mines in China and the former Soviet Union should be included in future work.

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64 Phosphorus trichloride

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64.1 Introduction

Phosphorus trichloride (PCl_3 , CAS-No. 7719-12-2) is at room temperature a clear, volatile liquid that can be hydrolyzed rapidly by water (Riess (2000)). Phosphorus trichloride is soluble in benzene, chloroform, carbon tetrachloride and diethyl ether. For this inventory the functional unit is 1 kg liquid phosphorus trichloride. The most important chemical and physical properties of phosphorus trichloride used in this inventory are given in here.

Synonyms for phosphorus trichloride: -

Tab. 64.1 Chemical and physical properties of phosphorus trichloride (according to Riess (2000))

Property	Unit	Value	Remarks
Molecular weight	g mol^{-1}	137.33	
Boiling point	°C	76.1	at normal pressure
Melting point	°C	-93.6	at normal pressure

64.2 Reserves and Resources of material

The production of phosphorus trichloride is made by the combustion of phosphorus in a dry steam of chlorine (for more details see chapter ‘system characterization’). Therefore, all further discussion of resources equals to the discussion in the respective chapters of this report about phosphorus resp. chlorine.

64.3 Use of material / product

According to Riess (2000), phosphorus trichloride is the starting material for the production of the different organophosphorus compounds. It is the starting material for the production e.g. of phosphoryl chloride, phosphorus pentachloride or phosphonic acid. Besides, phosphorus trichloride is also used as an important intermediate in the production of insecticides as well as a chlorinating agent or catalyst in organic chemistry.

The worldwide production capacity of phosphorus trichloride in 1989 was estimated to be in the order of > 300 kt. Its consumption was in the same year in the order of 170 kt. Further details about the production – e.g. the amounts produced in Europe – were not available (Riess (2000)).

64.4 Systems characterization

In the production process for phosphorus trichloride the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of phosphorus trichloride is not considered to be high. For this inventory the functional unit is 1 kg of liquid phosphorus trichloride. As process location Europe (RER) is used.

According to Riess (2000), phosphorus combustion in a chlorine stream produces phosphorus trichloride. Therefore molten white phosphorus and gaseous chlorine react in already produced phosphorus

trichloride. The reaction is exothermic and this reaction heat can be used to keep the system at its boiling point, allowing to distill off the produced phosphorus trichloride. After cooling down this product in air-cooled condensers, no further treatment steps are needed (there is no free phosphorus within the product).

64.5 Phosphorus trichloride, at plant (Location: RER)

64.5.1 Process

This dataset includes a rough estimation of the production process for phosphorus trichloride. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The above described production way for phosphorus trichloride can be summarized within the following reaction equation:



64.5.2 Resources

Energy

According to Riess (2000), no external heat energy is needed within the process. Nevertheless, in order not to neglect the electricity demand of the phosphorus trichloride synthesis, this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). There, 38% of the 3.2 MJ kg⁻¹ of total energy consumed is electricity. Therefore, for this inventory an amount of 1.2 MJ kg⁻¹ electricity was used.

Raw materials and Chemicals

According to the above shown reaction equations - the following stoichiometric inputs are needed (yield 100%) for the production of 1 kg of phosphorus trichloride:

- phosphorus, P₄: 225.587 g (1.82 mol)
- chlorine, Cl₂: 774.180 g (10.92 mol)

For the production – due to the fact that Riess (2000) describes a continuous process - a yield of 100% for the combustion of phosphorus and of 98% for chlorine is assumed in this study. Therefore 225.587 g white phosphorus and 789.98 g chlorine are considered as raw materials in this inventory. A summary of the values used is given in Tab. 64.2.

Water use

There was no information available on the amount of cooling water used within the plant – actually, the cooling system is an air-cooled condenser. Therefore, it is assumed in this study that no cooling water is used.

For the process water amount, due to the fact that it is a combustion reaction, it is also assumed that there is no water input.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg phosphorus trichloride was included.

64.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg phosphorus trichloride is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of phosphorus trichloride. As approximation the air emissions occurring in the different stages of the production were estimated to 0.2% of the raw material input.

This assumption leads to air emissions of 0.451 g phosphorus and 1.548 g of chlorine.

Emissions to water

As no water is consumed, also no emissions to water can occur within this study.

Solid wastes

Solid wastes occurring during the production of phosphorus trichloride were neglected in this inventory.

Tab. 64.2 Energy demand, Resource demand and emissions for the production of phosphorus trichloride.

[per kg phosphor trichloride]	Remark		
INPUTS			
phosphorus (white phosphor)	kg	0.226	stoechiometric calc., 100% yield
chlorine	kg	0.790	stoechiometric calc., 98% yield
Electricity, medium voltage	kWh	0.333	estimation
transport by train	tkm	6.09E-01	calculated with standard distances
transport by lorry	tkm	1.02E-01	calculated with standard distances
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
phosphor, to air	kg	4.51E-04	estimated as 0.2% of input
chlorine, to air	kg	1.55E-03	estimated as 0.2% of input

64.6 Data quality considerations

The following table shows the data quality indicators for the inventory of phosphorus trichloride production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the phosphorus trichloride production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the electricity demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 64.9.

Tab. 64.3 Input / Output and uncertainty for the process “phosphorus trichloride, at plant (RER)”

Explanation	Name	Location	Unit	<i>phosphorous chloride, at plant</i>	uncertaintyType	standardDeviation95%	GeneralComment	
							Location	RER
							Infrastructure	0
							Unit	kg
Input from Technosphere	phosphorus, white, liquid, at plant	RER	kg	2.26E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	chlorine, liquid, production mix, at plant	RER	kg	7.90E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant	
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation	
	transport, freight, rail	RER	tkm	6.09E-01	1	2.09	(4,5,na,na,na,na); standard distances	
	transport, lorry 32t	RER	tkm	1.02E-01	1	2.09	(4,5,na,na,na,na); standard distances	
Output Air emission	phosphorous chloride, at plant	RER	kg	1				
	Heat; waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input	
	Chlorine		kg	1.55E-03	1	2.32	(5,5,na,na,na,5); estimation	
	Phosphorus		kg	4.51E-04	1	2.32	(5,5,na,na,na,5); estimation	

64.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

64.8 Conclusions

The inventory for phosphorus trichloride is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if phosphorus trichloride is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

64.9 EcoSpold Meta Information

ReferenceFunction	401	Name	phosphorous chloride, at plant
Geography	662	Location	RER
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	402	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	404	Amount	1
ReferenceFunction	490	LocalName	Phosphortrichlorid, ab phosphorus trichloride
ReferenceFunction	491	Synonyms	
ReferenceFunction	492	GeneralComment	The functional unit represent 1 kg of liquid phosphorus chloride. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	502	CASNumber	7719-12-2
TimePeriod	601	StartDate	2000
TimePeriod	602	EndDate	2000
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	date of published literature
Geography	663	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	692	Text	Production of phosphorus trichloride by combustion of phosphorus in a chlorine stream with a overall yield of 100% for phosphorus (due to fact that a continuous process) resp. 98% for chlorine. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) were estimated.
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	
Representativeness	725	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	726	Extrapolations	
Representativeness	727	UncertaintyAdjustments	none

64.10 References

- Frischknecht et al. (2007) Frischknecht R., Althaus H.-J., Doka G., Dones R., Hischier R., Hellweg S., Jungbluth N., Kellenberger D., Nemecek T., Rebitzer G. and Spielmann M. (2007) Overview and Methodology. Final report ecoinvent Data v2.0 No. 1. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.
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65 Phthalic anhydride

Author: Roland Hischier, EMPA St. Gallen
 Review: Heiko Kunst, TU Berlin

65.1 Introduction

Phthalic anhydride ($C_8H_4O_3$, CAS-No. 85-44-9) forms at room temperature colorless needles with a monoclinic or rhombic crystalline form (Lorz et al. (2000)). Phthalic anhydride is 100% miscible with organic solvents like Benzene or Ethanol while in water it is only partially miscible. For this inventory the functional unit is 1 kg solid phthalic anhydride. The most important chemical and physical properties of this substance used in this inventory are given here.

Synonyms for phthalic anhydride: isobenzofuran-1,3-dione

Tab. 65.1 Chemical and physical properties of methyl ethyl ketone (according to Lorz et al. (2000))

Property	Unit	Value	Remarks
Molecular weight	148.12	$g\ mol^{-1}$	
Boiling point	295.1	°C	at normal pressure
Melting point	131.6	°C	at normal pressure

65.2 Reserves and Resources of material

The production of phthalic anhydride is made nowadays predominantly by gas-phase oxidation of oxylene or naphthalene. Therefore, all further discussion of resources equals to the discussion about the oil reserves (see Dones et al. (2007)).

65.3 Use of material / product

According to Lorz et al. (2000), phthalic anhydride is mainly used for the production of plasticizers (about 55% of the total production volume). The remaining 45% are used for the production of unsaturated polyester resins, alkyd resins and various other processes.

In 1996, the worldwide production capacity of phthalic anhydride was more than 3.7 Mt. Thereof, only about 25% was situated in Western European countries – while Asia has about 30% of this capacity (Lorz et al. (2000)).

65.4 System characterisation

This chapter describes the data of the module “phthalic anhydride, at plant (RER)” in the ecoinvent database. The system refers to 1 kg of liquid phthalic anhydride and the process location is Europe. The system includes raw materials, auxiliaries, infrastructure and land use, transportation of the raw materials and wastes as well as the generation of solid wastes and emissions to air and water. It does not include transportation of the final product phthalic anhydride. There are no by-products generated in the production process.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emitted in the compartment “high population density”. The emissions into water are assumed to be emitted into a river. Furthermore, it is assumed that 100% of the electricity consumed is converted to waste heat, and that 100% of the waste heat is released to the air.

65.5 Phthalic anhydride, at plant (location: RER)

65.5.1 Process data

The data source for this study is von von Däniken & Chudacoff (1995), a survey from the Swiss Agency for the Environment, Forests and Landscape (BUWAL) where an environmental assessment of this varnish is performed. The source of the data is a Dutch study from 1992 as well as the US soft drink packaging study from Franklin concerning the emission and waste amounts (using the production of terephthalic acid as a proxy).

65.5.2 Raw materials and auxiliaries

According to von von Däniken & Chudacoff (1995), for the manufacturing of 1 kg phthalic anhydride 0.95 kg of o-xylol are needed. No further raw materials or auxillaries are mentioned.

65.5.3 Energy and transportation

According to the source mentioned, an energy input of 0.5 kWh of electricity as well as 7.5 MJ heat is needed for the production process. The heat is further split to 31.1% coal, 4.1% light fuel oil, 18.3% heavy fuel oil and 46.5% natural gas. As the dataset in von Däniken & Chudacoff (1995) contains not very detailed information about air emissions, the respective heating modules are used here. Concerning the electricity, the UCTE mix is used.

In regard to transportation of raw materials, no information about distances is available in the examined data source. Therefore, standard distances as defined in Frischknecht et al. (2007) were used: 100 km by lorry 32t and 600 km by train.

65.5.4 Infrastructure and land use

There is no information available about infrastructure and land-use. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. For this dataset, the infrastructure value is $4 * 10^{-10}$ unit per kg of phthalic anhydride.

65.5.5 Solid wastes and emissions to air and water

Within the ecoinvent project, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. All other emission and waste information is taken from von Däniken & Chudacoff (1995). These data together with the assumptions used for the integration into the ecoinvent database are summarized in the following table.

Tab. 65.2 Emission and waste information for the production of phthalic anhydride

[g/kg phthalic anhydrid]	amount	remarks for integration
<i>to air</i>		
dust	0.27	Assumption: 75% <2.5 0m, 25%>10 0m
Sulphur dioxide (as SO _x)	1.76	-
Carbon monoxide	6.96	as carbon dioxide, fossil
Hydrocarbons, unspecified	1.93	as NMVOC, unspecified
Other organics ¹	2.69	as NMVOC, unspecified
Nitrogen oxides (as NO _x)	0.4	-
<i>to water</i>		
BOD, biological oxygen demand	0.11	-
COD, chemical oxygen demand	0.63	-
suspended solids	0.18	-
ammonium, NH ₄ ⁺	0.34	-
<i>waste</i>		
unspecified waste	0.05	as "disposal, municipal solid waste, to sanitary landfill"

¹ The emission „other organics“ is mentioned in von Däniken 1995 as „carcinogens“, in the original publication of Franklin it is mentioned as „other organics“ – thus the latter expression is used for the ecoinvent project.

65.6 Data quality considerations

The following table shows the data quality indicators for the inventories of phthalic anhydride production described above. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data are based on Dutch producers, representing the beginning of the 90s and are reported in a Swiss EPA report (von Däniken & Chudacoff (1995)). Thus they have a certain level of uncertainty. Higher uncertainties have the transport amounts and the infrastructure as they are based only on an approximation because of missing data.

Tab. 65.3 Input- / Output data and uncertainties for the dataset “phthalic anhydride, at plant (RER)”

Explanation	Name	Location	Unit	phthalic anhydride, at plant		standardDeviation95%	GeneralComment
				RER	o kg		
				Location	InfrastructureProcess Unit		
Input from Technosphere	xylene, at plant	RER	kg	9.50E-01	1	1.25	(2,3,3,1,1,5); data from literature (von Däniken 1995)
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	5.00E-01	1	1.25	(2,3,3,1,1,5); data from literature (von Däniken 1995)
	natural gas, burned in industrial furnace >100kW	RER	MJ	3.49E+00	1	1.25	(2,3,3,1,1,5); data from literature (von Däniken 1995)
	light fuel oil, burned in industrial furnace 1MW, non-modulating	RER	MJ	3.08E-01	1	1.25	(2,3,3,1,1,5); data from literature (von Däniken 1995)
	heavy fuel oil, burned in industrial furnace 1MW, non-modulating	RER	MJ	1.37E+00	1	1.25	(2,3,3,1,1,5); data from literature (von Däniken 1995)
	hard coal, burned in industrial furnace 1-10MW	RER	MJ	2.33E+00	1	1.25	(2,3,3,1,1,5); data from literature (von Däniken 1995)
	transport, freight, rail	RER	tkm	5.70E-01	1	2.09	(4,5,na,na,na,na); standard distances
	transport, lorry 32t	RER	tkm	9.50E-02	1	2.09	(4,5,na,na,na,na); standard distances
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation
	phthalic anhydride, at plant	RER	kg	1			
Output Air emission	Heat, waste	MJ	1.80E+00	1	1.25		(2,3,3,1,1,5); calculated from electricity input
	Carbon monoxide, fossil	kg	6.96E-03	1	5.07		(2,3,3,1,1,5); data from literature (von Däniken 1995)
	Particulates, < 2.5 um	kg	2.03E-04	1	3.06		(2,3,3,1,1,5); data from literature (von Däniken 1995)
	Particulates, > 2.5 um, and < 10um	kg	6.75E-05	1	2.07		(2,3,3,1,1,5); data from literature (von Däniken 1995)
	Sulfur dioxide	kg	1.76E-03	1	1.25		(2,3,3,1,1,5); data from literature (von Däniken 1995)
	Nitrogen oxides	kg	4.00E-04	1	1.58		(2,3,3,1,1,5); data from literature (von Däniken 1995)
	NM VOC, non-methane volatile organic compounds, unspecified origin	kg	4.62E-03	1	1.58		(2,3,3,1,1,5); data from literature (von Däniken 1995)
Water emission	BOD5, Biological Oxygen Demand	kg	1.10E-04	1	1.58		(2,3,3,1,1,5); data from literature (von Däniken 1995)
	COD, Chemical Oxygen Demand	kg	6.30E-04	1	1.58		(2,3,3,1,1,5); data from literature (von Däniken 1995)
	Suspended solids, unspecified	kg	1.80E-04	1	1.58		(2,3,3,1,1,5); data from literature (von Däniken 1995)
	Ammonium, ion	kg	3.40E-04	1	1.58		(2,3,3,1,1,5); data from literature (von Däniken 1995)

65.7 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

65.8 Conclusions

Average European datasets for the production of phthalic anhydride based on Dutch data are established. The dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on a report covering various Dutch companies, based on statistics from the beginnin of the 1990s. The data are thus of a intermediate quality and can be used accordingly.

65.9 EcoSpold Meta Information

ReferenceFunction	Name	phthalic anhydride, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw material and energy input, estimation of air emissions by using analogy to other process. Transports and Infrastructure estimated. Further inputs and solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Phthalsäureanhydrid, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of phthalic anhydride.
ReferenceFunction	CASNumber	
TimePeriod	StartDate	1995
TimePeriod	EndDate	1995
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of publication of used literature
Geography	Text	Data used are based actually on a Dutch and a US study. Data are used as European average data.
Technology	Text	no information given - assuming average Dutch technology in mid 90s
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	literature and estimations out of similar processes
Representativeness	Extrapolations	see geography
Representativeness	UncertaintyAdjustments	none

65.10 References

Dones et al. (2007)

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66 Polyester resin, unsaturated

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66.1 Introduction

Unsaturated polyester resins (according to Krämer (1992) they can be abbreviated as UP resins) are the product from a polycondensation of dicarboxylic acids (saturated, unsaturated) with glycols (Koo-Ling et al. (2002)). The specific properties depends on the types of acids and glycols used as well as on the proportions between these different educts (Koo-Ling et al. (2002)).

A discussion of resources equals to a discussion about the oil reserves (see Dones et al. (2007)).

66.2 Use of material / product

According to Krämer (1992), the majority of all UP resins is used in a reinforced (with glass fibers) form. The most important uses of UP resins are the automobile construction sector (parts for special-order vehicles), the building industry (doemlight crows, facade elements, cellar window frames), the electrical industry (molded parts e.g. for cable distribution cupboards) and the boat and ship building (construction material for boats).

In 2001, Western Europe, Japan and North America together had a production capacity of about 1.55 Mt – a value that will grow to 1.9 Mt by 2006 (Koo-Ling et al. (2002)).

66.3 System characterisation

This chapter describes the data of the module “polyester resin, unsaturated, at plant (RER)” in the ecoinvent database. The system refers to 1 kg of polyester resin, unsaturated and the process location is Europe. The system includes raw materials, auxiliaries, infrastructure and land use, transportation of the raw materials and wastes as well as the generation of solid wastes and emissions to air and water. It does not include transportation of the final product polyester resin, unsaturated. There are no by-products generated in the production process.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised are emitted in the compartment “high population density”. The emissions into water are assumed to be emitted into a river. Furthermore, it is assumed that 100% of the electricity consumed is converted to waste heat, and that 100% of the waste heat is released to the air.

66.4 Polyester resin, unsaturated, at plant (location: RER)

The data source for this study is the information found in Krämer (1992), describing the production of different types of unsaturated polyester resins. No quantitative information is available there. Based on the personal communication of EMPA Dübendorf²¹, as well as the assumption, that the production of alcylic resins is similar to the production here and thus the energy input as well as the emissions can be taken over, the dataset shown in xy can be established.

²¹ Personal communication from Hans-Jörg Althaus, EMPA Dübendorf from 19.11.02

Tab. 66.1 Emission and waste information for the production of polyester resin, unsaturated

[per kg polyester resins, unsaturated]		Remark
INPUTS		
Adipic acid	kg	0.146
Acetic anhydride	kg	1.0E-01
ethylene glycol	kg	0.1922
phthalic anhydride	kg	0.592
propylene glycol	kg	0.304
natural gas, burned in industrial furnace	MJ	1.42
light fuel oil, burned in industrial furnace	MJ	0.125
heavy fuel oil, burned in industrial furnace	MJ	0.56
coal, burned in industrial furnace	MJ	0.95
electricity	kWh	1.30E-02
OUTPUTS		
waste, heat	MJ	4.68E-02
COD, to water	kg	2.00E-03

Therefore, the following assumptions are used to harmonize this dataset as much as possible with the other datasets of the ecoinvent project:

- **Material input:** The above mentioned amounts of the different raw materials are used here.
- **Energy demand:** For the heat production, the distribution to the different types of fuels is given in von Däniken & Chudacoff (1995). As the dataset in von Däniken & Chudacoff (1995) contains not very detailed information about air emissions, the respective heating module is used for the consumption of the different fuels. Concerning the electricity mix, the UCTE-mix is used.
- **Transports:** All materials used have to be transported to the production site. Therefore, the standard distances and means according to Frischknecht et al. (2007) are used for. In case of the fuels these transport amounts are already included in the used “heating” modules.
- **Infrastructure and the land-use** For the infrastructure the modules of the organic chemicals plant, described in, Althaus et al. (2003) is used. Assuming a total life-span of 50 years, an amount of 4.0E-10 units of the infrastructure per kg fatty acid is calculated.
- **Water input and output:** No information is given in this data source. For the cooling water, the amount of the chemical plant (Gendorf (2000)) already used in other modules of this paragraph is used. In this plant an average of 24 kg water per kg of product were used for. Accordingly this amount is added to the above shown datasets. For the process water 25% of this amount is added.
- **Emissions:** Apart a COD value for the waste water, no further emissions from the process itself are known, and the emissions from the combustion processes are included in the chosen “heating” module. According to the methodology of the ecoinvent project, the input of electricity is shown as waste heat output to the air.
- **Waste:** No waste reported, thus no waste assumed.

66.5 Data quality considerations

Tab. 66.2 summarizes the uncertainty scores established according to the method used in the ecoinvent project (see) Frischknecht et al. (2007), including reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. The data are based on literature, personal communication and the similarity to the acrylic resin production (von Däniken & Chudacoff (1995)).

Tab. 66.2 Input- / Output data and uncertainties for the dataset “polyester resin, unsaturated, at plant (RER)”

Explanation	Name	Location	Unit	polyester resin saturated, at plant	RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment	
								Location	InfrastructureProcess Unit
Resources Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5.5,1,1,4,5); data based on consumption of 1 big company (5.5,1,1,4,5); assumption		
	Water, unspecified natural origin		m3	6.00E-03	1	1.88			
	ethylene glycol, at plant	RER	kg	1.92E-01	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	adipic acid, at plant	RER	kg	1.46E-01	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	acetic anhydride, at plant	RER	kg	1.00E-01	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	phthalic anhydride, at plant	RER	kg	5.92E-01	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	propylene glycol, liquid, at plant	RER	kg	3.04E-01	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.30E-02	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	natural gas, burned in industrial furnace >100kW	RER	MJ	1.42E+00	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	light fuel oil, burned in industrial furnace 1MW, non-modulating	RER	MJ	1.25E-01	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	heavy fuel oil, burned in industrial furnace 1MW, non-modulating	RER	MJ	5.60E-01	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	hard coal, burned in industrial furnace 1-10MW	RER	MJ	9.50E-01	1	1.41	(3.5,3,1,3,5); personal communication, based on literature		
	transport, freight, rail	RER	tkm	8.01E-01	1	2.09	(4.5,na,na,na,na); standard distances		
	transport, lorry 32t	RER	tkm	1.33E-01	1	2.09	(4.5,na,na,na,na); standard distances		
Output Air emission Water emission	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4.5,1,3,5,4); estimation		

66.6 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

66.7 Conclusions

The inventory for unsaturated polyester resin is based on expert estimations and assumptions. The unit process raw data are meant to be used as background information if this resin is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

66.8 EcoSpold Meta Information

ReferenceFunction	Name	polyester resin saturated, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Estimated raw material input. Energy input and emissions to water by analogy to other process. Transports and Infrastructure estimated. Further inputs and solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Polyesterharz gesättigt, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of polyester resin, unsaturated.
ReferenceFunction	CASNumber	
TimePeriod	StartDate	1995
TimePeriod	EndDate	2002
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	Data used has no specific geographical origin (general information about composition). Data are used as European average data.
Technology	Text	data represents a mix of most often used substances for the production of polyester resin
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	literature, expert knowledge and estimations out of similar processes
Representativeness	Extrapolations	see geography and
Representativeness	UncertaintyAdjustments	none

66.9 References

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67 Polytetrafluoroethylene (PTFE), Trichloromethane, Chlorodifluoromethane and PTFE-Film

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Last update v2.1, 2007

Acknowledgement

We thank an important producer of PTFE for some information provided in a personal communication.

Summary

This chapter describes the production of polytetrafluoroethylene (PTFE). The intermediate production stages of trichloromethane and chlorodifluoromethane production are included in the investigation. The inventory for PTFE and some of the pre-products is based on a literature research, general information provided by manufacturers and assumptions. The unit process raw data are meant to be used as background information if PTFE or PTFE film is used for a product in small amounts. Therefore these data can give an approximation. These are not reliable enough for direct comparison of this material with alternative products.

67.1 Introduction

This chapter describes the production of polytetrafluoroethylene. This product is better known under the brand names like Teflon® or Fluon. A common abbreviation is PTFE. It can be used for a range of different applications. In the context of this project the use as films on solar glass for solar collectors (Jungbluth 2003b) is the main point of interest. The pre-products trichloromethane and chlorodifluoromethane are also investigated.

67.2 Reserves and Resources of PTFE

PTFE is a solid organic chemical product. Basic resources are raw salt and fluorite. Manufacturers of PTFE include Ausimont (Algoflon and Halar), Daikin Kogyo (Polyflon), Du Pont (Teflon®), Hoechst (Hostaflon), ICI (Fluon), and a producer in Russia (Ftoroplast) (Asahi 2002; Ausimont 2002; DuPont 2002). The worldwide production capacity in 1987 for all fluoroplastics was about 45 000t (Carlson & Schmiegel 2002).

67.3 Characterisation of PTFE

Polytetrafluoroethylene (PTFE, CAS number 009002-84-0) is a straight-chain polymer of tetrafluoroethylene (TFE). It has a high melting point (327°C) and a maximum use temperature (>260°C). PTFE exhibits unusual toughness down to very low temperatures. It is insoluble in all known solvents and resists attack by most chemicals. PTFE has the general formula (Carlson & Schmiegel 2002):



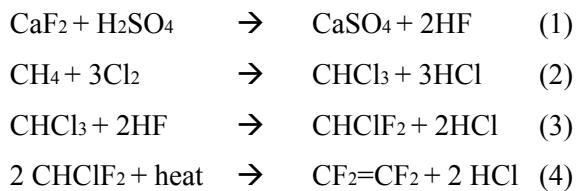
The product of interest for this study is fluorocarbon film used for coatings of solar glass. It is a transparent, thermoplastic film that can be heat sealed, thermoformed, vacuum formed, heat bonded, welded, metalized, laminated-combined with dozens of materials, and can also be used as an excellent hot-melt adhesive (DuPont 2002).

67.4 Use of PTFE

Numerous uses have been found for fluoropolymers, many of which cannot be satisfied by any other material. About half of the PTFE resin that is produced is used in electrical applications such as insulation, flexible printed circuits, and piezoelectric devices. Other applications include chemically resistant coatings, bearings, no-stick surfaces, architectural fabric, laboratory ware, heat exchangers and water repellent fabrics (Carlson & Schmiegel 2002). PTFE products are offered in a broad range of grades including granular fine cut, free flows, compounds, fine coagulated powders, and aqueous dispersions.

67.5 System Characterisation

Fig. 67.1 shows a flow chart for the production of fluorochemicals and PTFE. The following chemical reactions are used to create the monomers (Cedergren et al. 2001):



Parts of the production are carried out at high pressure and high temperature, 590 °C – 900 °C. The first reaction (1) takes place in the presence of heat and HSO_3^- and steam. The inventory for the production of hydrogen fluoride for this project can be found in the report (Jungbluth 2003a). Reaction (2) is used to produce trichloromethane. Reaction 3 for the production of chlorodifluoromethane takes place in the presence of a catalyst. The production of PTFE (4) takes place under high temperature pyrolysis conditions.

Large amounts of hydrochloric acid (HCl) are generated as a couple product during the process and are sold as a 30% aqueous solution. A large number of other by-products and emissions is formed in the processes (benzene, dichloromethane, ethylene oxide, formaldehyde, R134a, and vinyl chloride) and small amounts of the highly toxic perfluoroisobutylene $\text{CF}_2=\text{C}(\text{CF}_3)_2$. The by-products in the production of monomers can harm the processes of polymerisation. Because of this the refinement of the production of monomers has to be very narrow. This makes the process complex and it contributes to a high cost for the PTFE-laminates. (Cedergren et al. 2001).

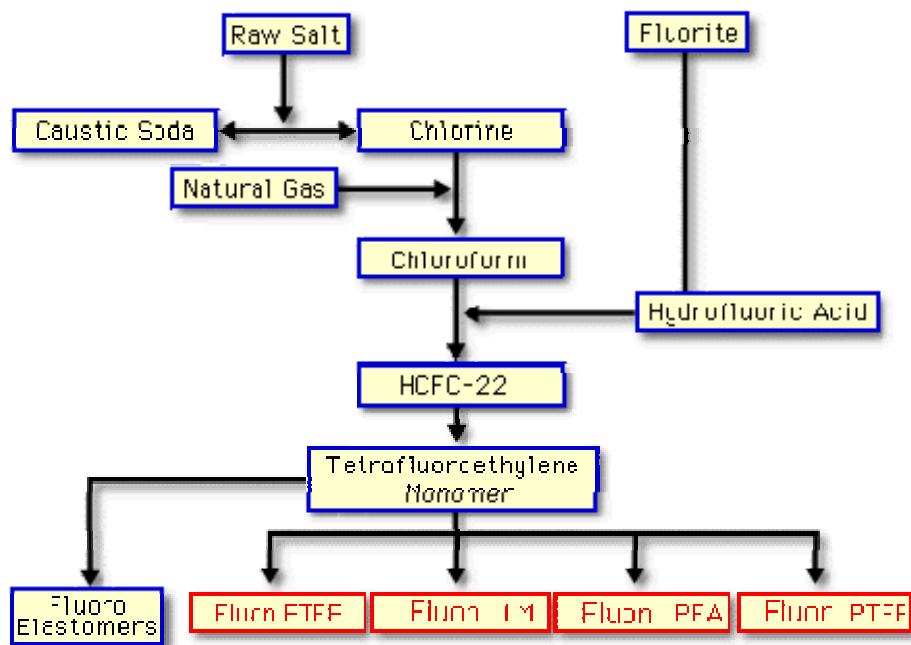


Fig. 67.1 Flow chart for the production of fluoro chemicals and PTFE (Asahi 2002)

The principal method for synthesizing organic fluoropolymers is free-radical polymerisation (Carlson & Schmiegel 2002). PTFE is obtained by polymerisation of the tetrafluoroethylene monomer. This reaction generally takes place in an aqueous medium with additional additives and modifiers. The polymerisation process requires a lot of energy to reach the reaction temperature, but it is about the same amount of energy is liberated in the exothermic reaction. Two basic polymerisation processes are used in order to obtain two different classes of polymers, which are also processed by different techniques (Ausimont 2002):

- Suspension polymerisation: resulting polymers are suitable for moulding or ram extrusion after appropriate treatment.
- Dispersion polymerisation: resulting aqueous dispersion of polymers, after concentration and formulation, can be used for impregnation, cast films, dedusting and coating. Coagulated powders obtained from aqueous dispersion are used in paste extrusion technology.

67.6 Life Cycle Inventory for PTFE

Specific data for the product of interest in this context, the fluorocarbon film materials were not available. A life cycle inventory for PTFE laminates has been elaborated by (Cedergren et al. 2001). It is mainly based on stoichiometric assumptions for the production process. The intermediate products chlorodifluoromethane (HCFC-22) and trichloromethane (chloroform) have been investigated by (Frischknecht 1999). The cumulative results of a life cycle inventory for PTFE have been provided by a manufacturer. This study is confidential. Some information could be used in estimating and verifying the assumptions for the life cycle inventory. But the data shown here are not specific or original data of a company.

Environmental impacts and exchanges are fully allocated to the main products of the processes. The couple product HCl which is formed in the process stages contributes only a small share to the earnings of the process. The ratios in selling prices of the two products are: HCl : chlorodifluoromethane = 2.8 : 97.2 and HCl : PTFE = 0.5 : 99.5. Trichloromethane is an intermediate raw material that is not

sold on the market (and thus has no clear price).²² From an economic point of view its production can thus be neglected even if the mass share is relative high.

67.6.1 Trichloromethane

The unit process raw data for the production of trichloromethane (CAS No. 67-66-3) are shown in Tab. 67.3. It is produced as a clear colourless liquid with a pleasant, sweet odour. The chemical is an intermediate product for e.g. chlorodifluoromethane product and thus not sold on the market. The dataset has been elaborated by (Frischknecht 1999). It is based on stoichiometric assumptions and a literature information for the energy use (Papasavva & Moomaw 1998). Natural gas is assumed as an input instead of methane. Transports of chlorine are not considered because it is assumed that the production takes place in the same plant. Data for infrastructure are assumed with generic data. The couple product HCl (0.92kg/kg) is not considered in the calculation.

Tab. 67.1 Unit process raw data and data quality indicators for production of trichloromethane.

	Name	Locati	on	Unit	trichloromethane,	Under	Stand	at De	vatio	GeneralComment
	Location	Infrastru			RER	Stand	at De	vatio		
	Infrastructure	Process	Unit		0	at De	vatio			
product	trichloromethane, at plant	RER	0	kg	1.00E+0					
technosphere	natural gas, high pressure, at consumer	RER	0	MJ	7.65E+0	1	1.38	(4,5,1,1,3,na); Assumption for methane, stoichiometric calculation, yield 85%		
	electricity, medium voltage, production UCTE, at grid	UCTE	0	kWh	4.44E-1	1	1.32	(3,5,1,1,3,na); Literature 1998, estimation 10% electricity		
	natural gas, burned in industrial furnace >100kW	RER	0	MJ	1.10E+1	1	1.32	(3,5,1,1,3,na); Literature 1998, estimation 90% gas		
	chlorine, liquid, production mix, at plant	RER	0	kg	8.48E-1	1	1.38	(4,5,1,1,3,na); Stoichiometric calculation, yield 85%, not including Cl2 for total HCl couple product		
	chemical plant, organics	RER	1	unit	4.00E-10	1	3.90	(5,na,1,1,5,na); Generic estimation		
emission air, high population density	Methane, tetrachloro-, CFC-10	-	-	kg	1.00E-3	1	1.88	(5,5,1,1,3,na); Estimation of 0.1% emission		
	Chloroform	-	-	kg	1.00E-2	1	1.88	(5,5,1,1,3,na); Estimation of 1% emission		
	Methane, dichloro-, HCC-30	-	-	kg	3.00E-4	1	1.88	(5,5,1,1,3,na); Estimation of 0.03% emission		
	Ethene, chloro-	-	-	kg	5.00E-7	1	1.88	(5,5,1,1,3,na); Estimation		
	Heat, waste	-	-	MJ	1.60E+0	1	1.88	(5,5,1,1,3,na); Estimation of 1% emission		
emission water, river	Methane, dichloro-, HCC-30	-	-	kg	5.00E-6	1	3.32	(5,5,1,1,3,na); Estimation		
couple product	hydrochloric acid, 36% in H ₂ O, at plant			kg	9.20E-1					
total couple product for PTFE	hydrochloric acid, 36% in H ₂ O, at plant			kg	1.21E+0					

67.6.2 Chlorodifluoromethane

Chlorodifluoromethane (CAS No. 75-45-6), a non-flammable gas, is created by reacting chloroform with hydrogen fluoride in the presence of an antimony pentachloride catalyst. The gaseous reactants are sent to a reactor where they are bubbled through the molten catalyst. The product gas is then cooled and the unreacted chloroform is separated and recycled. Scrubbers absorb the HCl by using water, NaOH and sulphuric acid. The product gas is then converted into a liquid by refrigeration and sent to a series of distillation columns where trifluoromethane is removed from the product stream (Overcash n.d.).

The unit process raw data for the production of chlorodifluoromethane are shown in Tab. 67.2. Inventory datasets have been elaborated by (Frischknecht 1999; Overcash n.d.). The inventories are based on some literature data. Data for infrastructure are assumed with generic data. (Harnisch & Hendriks 2000) give an emission factor of 1.5% to 4% for HFC-23 as a by-product of HCFC-22 production. (Ros 1994) reported a much lower value (0.35%) for the production plant of DuPont in the Netherlands. A thermal destruction device at this place removes a large part of the by-products, e.g. 94% of the HFC-23. This value has been taken to account for the production at a modern plant in Europe and not for the world average. Standard transport distances have been considered for this study. The ratios in selling price of the two products are: HCl : chlorodifluoromethane = 2.8 : 97.2. The by-products HCl (0.367kg/kg) and trifluoromethane are not considered in the calculation.

²² Information provided by an important producer of PTFE in a personal communication, 11.2002.

Tab. 67.2 Unit process raw data and data quality indicators for production of chlorodifluoromethane.

	Name	Location	Unit	Infrastructure	chlorodifluoromethane, at plant	Uncert. Stand. dev. ratio	GeneralComment	chlorodifluoromethane, at plant	chlorodifluoromethane, at plant
	Location	Unit	Infrastructure	Process Unit	NL 0 kg	NL 0 kg		NL 0 kg	US 0 kg
product technosphere	chlorodifluoromethane, at plant	NL 0 kg	1.00E+0					1.00E+0	1.00E+0
	electricity, medium voltage, at grid	NL 0 kWh	5.00E-1		1 1.24 (3,3,1,1,1,5); Literature 1998			5.00E-1	3.37E-1
	natural gas, burned in industrial furnace >100kW	RER 0 MJ	2.00E+0		1 1.24 (3,3,1,1,1,5); Literature 1998			2.00E+0	1.24E+0
	tap water, at user	RER 0 kg	9.53E-1		1 1.26 (3,na,3,3,1,5); Calculation in literature (3,3,1,1,1,5); Estimation based on literature values			9.53E-1	
	hydrogen fluoride, at plant	GLO 0 kg	5.50E-1		1 1.24 (3,na,3,3,1,5); Calculation in literature			5.00E-1	6.16E-1
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER 0 kg	6.16E-2		1 1.26 (3,na,3,3,1,5); Calculation in literature				6.16E-2
	sulphuric acid, liquid, at plant	RER 0 kg	2.13E-1		1 1.26 (3,na,3,3,1,5); Calculation in literature				2.13E-1
	trichloromethane, at plant	RER 0 kg	1.60E+0		1 1.24 (3,3,1,1,1,5); Estimation based on literature values			1.54E+0	1.68E+0
	chemical plant, organics	RER 1 unit	4.00E-10		1 3.90 (5,na,1,1,5,na); Generic estimation				
	transport, lorry >16t, fleet average	RER 0 tkm	2.42E-1		1 2.09 (4,5,na,na,na); Standard distance 100km			2.04E-1	2.57E-1
	transport, freight, rail	RER 0 tkm	1.45E+0		1 2.09 (4,5,na,na,na); Standard distance 600km			1.22E+0	1.54E+0
	disposal, refinery sludge, 89.5% water, to hazardous waste incineration	CH 0 kg	4.40E-3		1 1.31 (4,3,2,1,1,5); Chemical wastes, literature 1994			4.40E-3	-
	disposal, municipal solid waste, 22.9% water, to municipal incineration	CH 0 kg	1.20E-3		1 1.31 (4,3,2,1,1,5); Other wastes, literature 1994			1.20E-3	-
emission air, high population density	Methane, chlorodifluoro-, HCFC-22	- - kg	3.80E-3		1 1.61 (3,4,3,1,1,5); Range 0.38-5% of product, estimation for European plant.			3.80E-3	-
	Methane, trifluoro-, HCFC-23	- - kg	3.50E-3		1 1.61 (3,4,3,1,1,5); Range 0.35-1.5% of product, estimation for European plant.			3.50E-3	9.00E-4
	Methane, dichlorofluoro-, HCFC-21	- - kg	1.10E-5		1 1.58 (3,3,1,1,1,5); Data for European plant.			1.10E-5	2.10E-3
	Methane, trichlorofluoro-, CFC-11	- - kg	1.15E-5		1 1.58 (3,3,2,1,1,5); Literature 1994			1.15E-5	-
	Methane, dichlorodifluoro-, CFC-12	- - kg	8.20E-4		1 1.58 (3,3,2,1,1,5); Literature 1994			8.20E-4	-
	Chloroform	- - kg	1.00E-4		1 1.58 (3,3,2,1,1,5); Literature 1994			1.00E-4	8.40E-3
	Hydrogen fluoride	- - kg	3.10E-3		1 1.59 (3,na,3,3,1,5); Calculation in literature				3.10E-3
	Hydrogen chloride	- - kg	5.60E-3		1 1.59 (3,na,3,3,1,5); Calculation in literature				5.60E-3
	Heat, waste	- - MJ	1.80E+0		1 1.24 (3,3,1,1,1,5); Literature 1998			1.80E+0	1.21E+0
emission water, river	Chloroform	- - kg	1.10E-5		1 3.06 (3,3,2,1,1,5); Literature 1994			1.10E-5	-
	Antimony	- - kg	3.60E-5		1 5.07 (3,3,2,1,1,5); Literature 1994			3.60E-5	-
	Zinc, ion	- - kg	4.30E-6		1 5.07 (3,3,2,1,1,5); Literature 1994			4.30E-6	-
	Hydrocarbons, unspecified	- - kg	1.00E-6		1 3.06 (3,3,2,1,1,5); Literature 1994			1.00E-6	-
	Sodium, ion	- - kg	6.46E-2		1 5.08 (3,na,3,3,1,5); Calculation in literature				6.46E-2
	Chloride	- - kg	9.83E-2		1 5.08 (3,na,3,3,1,5); Calculation in literature				9.83E-2
	Sulfate	- - kg	2.78E-1		1 5.08 (3,na,3,3,1,5); Calculation in literature				2.78E-1
couple product	trifluoromethane	kg	1.78E-1						1.78E-1
	hydrochloric acid, 36% in H ₂ O, at plant	kg	3.67E-1					3.67E-1	7.21E-1
source								Frischkecht 1999	Oversch n.d.

67.6.3 PTFE

The unit process raw data for the production of PTFE are shown in Tab. 67.3. The inventory is based on a stoichiometric calculation and some assumptions for process specific emissions. Further information was available for a production plant in the Netherlands (Ros 1994). Information for the energy use was not available. It is estimated with 5MJ/kg. Data for infrastructure are assumed with generic data. The couple product HCl (0.18kg/kg) is not considered in the calculation.

Tab. 67.3 Unit process raw data and data quality indicators for production of PTFE.

	Name	Location	Unit	Infrastructure	tetrafluoroethylene, at plant	Uncert. Stand. dev. ratio	GeneralComment
	Location	Unit	Infrastructure	Process Unit	RER 0 kg		
product technosphere	tetrafluoroethylene, at plant	RER 0 kg	1.00E+0				
	natural gas, burned in industrial furnace >100kW	RER 0 MJ	5.00E+0		1 1.57 (5,na,na,3,na); Rough estimation (4,3,na,na,1,na); Stoichiometric calculation, 95% yield (4,3,3,1,1,5); Literature, Ros 1994,		
	chlorodifluoromethane, at plant	NL 0 kg	1.81E+0		1 1.22 (3,na,na,1,na); Stoichiometric calculation, 95% yield (4,3,3,1,1,5); Literature, Ros 1994,		
	disposal, refinery sludge, 89.5% water, to hazardous waste incineration	CH 0 kg	4.39E-3		1 1.33 (3,na,na,1,na); Chemical waste and waste with hydrocarbons		
	disposal, municipal solid waste, 22.9% water, to municipal incineration	CH 0 kg	1.22E-3		1 1.33 (4,3,3,1,1,5); Literature, Ros 1994, manufacturing waste		
	chemical plant, organics	RER 1 unit	4.00E-10		1 3.90 (5,na,1,1,5,na); Generic estimation (4,5,na,na,na,na); Standard distance 10/50km		
	transport, lorry >16t, fleet average	RER 0 tkm	2.32E-4		1 2.09 (4,3,na,na,1,na); Estimation 0.7% emission		
emission air, high population density	Ethane, 1,1,1,2-tetrafluoro-, HCFC-134a	- - kg	7.00E-3		1 2.05 (4,3,na,na,1,na); Literature		
	Methanol	- - kg	8.93E-3		1 2.05 (4,3,na,na,1,na); Literature		
	Methane, chlorodifluoro-, HCFC-22	- - kg	9.24E-2		1 2.05 (4,3,na,na,1,na); Literature, unspecified HCFC		
	Methane, trichlorofluoro-, CFC-11	- - kg	1.15E-5		1 2.05 (4,3,na,na,1,na); Literature		
	Methane, dichlorodifluoro-, CFC-12	- - kg	8.20E-4		1 2.05 (4,3,na,na,1,na); Literature		
couple product	hydrochloric acid, 36% in H ₂ O, at plant	kg	1.80E-1				
total couple product	hydrochloric acid, 36% in H ₂ O, at plant	kg	3.51E+0				

67.6.4 Adhesion of PTFE on Glass

Adhesion of PTFE to glass is difficult because it is usually undesirable to etch these substrates. In order to use PTFE for adhesion of glass, the surfaces to be coated shall be cleaned by boiling in isopropanol for 15 minutes, followed by drying. Then the dried surfaces are coated with a 2% solution of fluorosilane in 95% ethanol/5% water. The surface is baked at 110°C for 10 minutes and coated with a PTFE solution. The process can liberate vapours that may be dangerous for health. The isothermal rate of weight loss of PTFE in air at 360°C has been shown to be 0.2% to 0.6%/hr. Other decomposing products are HF, COF₂ (carbonyl fluoride), CO, and hexafluoroacetone (HFA). Some residual gases (incl. HF, COF₂, CO and HFA) diffuse from PTFE resins even at room temperature. Thus resin containers should be opened and used only in well-ventilated areas.²³ Emission figures were not available.

The unit process raw data for the adhesion of PTFE on glass are shown in Tab. 67.4. Quantitative data for this process were not available. The inventory has been estimated based on the information provided before. Data for infrastructure are assumed with generic data

Tab. 67.4 Unit process raw data and data quality indicators for adhesion of PTFE on glass.

product technosphere	Name	Locati on	Infrastr ucture	Unit	tetrafluoroethylene film, on glass	Uncert ain Stand ardDe viation	GeneralComment
	Location InfrastructureProcess Unit	RER	0	kg	RER 0 kg		
tetrafluoroethylene film, on glass	RER	0	kg	1.00E+0			
tetrafluoroethylene, at plant	RER	0	kg	1.05E+0	1 1.50 (5,na,1,1,1,na); Stoichiometric calculation, 95% yield		
silicone product, at plant	RER	0	kg	2.11E-5	1 1.50 (5,na,1,1,1,na); Rough estimation		
methanol, at regional storage	CH	0	kg	1.00E-3	1 1.50 (5,na,1,1,1,na); Rough estimation for alcohol		
isopropanol, at plant	RER	0	kg	1.00E-3	1 1.50 (5,na,1,1,1,na); Rough estimation		
natural gas, burned in industrial furnace >100kW	RER	0	MJ	5.00E+0	1 1.50 (5,na,1,1,1,na); Rough estimation		
chemical plant, organics	RER	1	unit	4.00E-10	1 3.90 (5,na,1,1,5,na); Generic data		
transport, lorry >16t, fleet average	RER	0	tkm	1.05E-1	1 2.09 (4,5,na,na,na,na); Standard distance 100km		
transport, freight, rail	RER	0	tkm	6.33E-1	1 2.09 (4,5,na,na,na,na); Standard distance 600km		
Hydrogen fluoride	-	-	kg	1.00E-4	1 1.77 (5,na,1,1,1,na); Rough estimation		
Carbon monoxide, fossil	-	-	kg	1.00E-4	1 1.50 (5,na,1,1,1,na); Rough estimation		
Acetone	-	-	kg	1.00E-4	1 2.23 (5,na,1,1,1,na); Rough estimation		

67.7 Data Quality Considerations

The simplified approach with a pedigree matrix has been used for calculating the standard deviation. The data quality is poor. A lot of assumptions has to be used to estimate the unit process raw data.

67.8 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database (www.ecoinvent.ch).

67.9 Conclusions

The inventory for PTFE-films, polytetrafluoroethylene and some of its pre-products is based on a literature research, general information provided by manufacturers and assumptions. The unit process raw data are meant to be used as background information if PTFE or PTFE film is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with alternative products.

²³ Information in the literature packet on Teflon® AF resin and solution provided by Du Pont, 5.2002.

Abbreviations

PTFE polytetrafluoroethylene

Appendices: EcoSpold Meta Information

67. Polytetrafluoroethylene (PTFE), Trichloromethane, Chlorodifluoromethane and PTFE-Film

ReferenceFunction	401 Name	trichloromethane, at plant	chlorodifluoromethane, at plant	tetrafluoroethylene, at plant	tetrafluoroethylene film, on glass
Geography	662 Location	RER	NL	RER	RER
ReferenceFunction	493 InfrastructureProcess	0	0	0	0
ReferenceFunction	403 Unit	kg	kg	kg	kg
DataSetInformation	201 Type	1	1	1	1
	202 Version	1.0	1.0	1.0	1.0
	203 energyValues	0	0	0	0
	205 LanguageCode	en	en	en	en
	206 LocalLanguageCode	de	de	de	de
DataEntryBy	302 Person	41	41	41	41
	304 QualityNetwork	1	1	1	1
ReferenceFunction	400 DataSetRelatesToProduct	1	1	1	1
	402 IncludedProcesses	Gate to gate inventory for the production, estimation for infrastructure and not including by-products.	Gate to gate inventory for the production, estimation for infrastructure and not including by-products.	Gate to gate inventory for the production, estimation for infrastructure and not including by-products.	Gate to gate inventory for the production, estimation for infrastructure.
	404 Amount	1	1	1	1
	490 LocalName	Trichloromethane, ab Werk	Chlorodifluoromethane, ab Werk	Tetrafluoroethylene, ab Werk	Tetrafluoroethyleneschicht, auf Glas
	491 Synonyms	Methyl trichloride // Chloroform // Refrigerant R20 // formyl trichloride // methane trichloride // methenyl trichloride // trichloroform // R 20 // r 20 (refrigerant) // Chloroform	HCFC-22 // Freon 22 // Algeon 22 // Isotron 22 // Difluorochloromethane // Monochlorodifluoromethane // Refrigerant R22 // Fluorocarbon 22 // Fisherbrand histo freeze(TM)-22 // R-22 // Freon R-22 // Halocarbon 22 // chlorodifluoromethane (R-22) // Chlorodifluoromethane	Fluon // PTFE // Teflon // Ethene // tetrafluoro- // homopolymer // Politef // Tetrafluoroethylene Resin	Fluon // PTFE // Teflon // Ethene // tetrafluoro- // homopolymer // Politef // Tetrafluoroethylene Resin
	492 GeneralComment	Inventory for a chemical.	Inventory for a chemical. Emissions of HFC-23 are much higher in the world wide average.	Inventory for a chemical.	Inventory for a chemical.
	494 InfrastructureIncluded	1	1	1	1
	495 Category	chemicals	chemicals	chemicals	chemicals
	496 SubCategory	organics	organics	inorganics	inorganics
	497 LocalCategory	Chemikalien	Chemikalien	Chemikalien	Chemikalien
	498 LocalSubCategory	Organisch	Organisch	Anorganika	Anorganika
	499 Formula	CHCl3	CHClF2	C2F4	C2F4
	501 StatisticalClassification	67-66-3	75-45-6	9002-84-0	9002-84-0
TimePeriod	502 CASNumber	1998	1999	1999	2002
	601 StartDate	1999	1999	1999	2002
	602 EndDate				
	603 DataValidForEntirePeriod	1	1	1	1
	611 OtherPeriodText	Publication date	Publication date	Publication date	Background information.
Geography	663 Text	Plant e.g. in NL	Plant e.g. in NL	Plant e.g. in NL	Production plant in RER
Technology	692 Text	Chemical processing	Chemical processing	Chemical processing	Chemical processing
Representativeness	722 Percent				
	724 ProductionVolume	The worldwide production capacity in 1987 for fluoroplastics was ca. 45 000t.	The worldwide production capacity in 1987 for fluoroplastics was ca. 45 000t.	The worldwide production capacity in 1987 for fluoroplastics was ca. 45 000t.	The worldwide production capacity in 1987 for fluoroplastics was ca. 45 000t.
	725 SamplingProcedure	Literature, company information, stoichiometric calculations, assumptions.	Literature, company information, stoichiometric calculations, assumptions.	Literature, company information, stoichiometric calculations, assumptions.	Own assumptions.
DataGenerator AndPublication	726 Extrapolations	none	none	none	none
	727 UncertaintyAdjustments	none	none	none	none
	751 Person	41	41	41	41
	756 DataPublishedIn	2	2	2	2
	757 ReferenceToPublishedSource	8	8	8	8
	758 Copyright	1	1	1	1
	759 AccessRestrictedTo	0	0	0	0
	760 CompanyCode				
	761 CountryCode				

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68 Propylene glycol

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68.1 Introduction

Propylene glycol ($\text{HOCH}_2\text{CH}(\text{CH}_3)\text{OH}$, CAS-No. 57-55-6) is at room temperature a clear, colourless, strongly hygroscopic liquid. For this inventory the functional unit is 1 kg liquid propylene glycol. The most important chemical and physical properties of propylene glycol used in this inventory are given here.

Synonyms for propylene glycol: 1,2-Propanediol

Tab. 68.1 Chemical and physical properties of propylene glycol

Property	Unit	Value	Remarks
Molecular weight	g mol^{-1}	76.10	
Vapour pressure	KPa	0.011	at 20 °C
Boiling point	°C	187.9	at normal pressure
Melting point	°C	< -60	at normal pressure

68.2 Reserves and Resources of material

The production of propylene glycol is made by direct hydrolysis of propylene oxide with water. Most production plants produce in the same time also di-propylene and tri-propylene glycol and separate all three by distillation (Sullivan (2000)). For this inventory, only the production of propylene glycol is investigated.

68.3 Use of material / product

According to Sullivan (2000), the most important use of propylene glycol is the production of unsaturated polyester resins and therefore ends up in automotive plastics, fibreglass boats and construction. Furthermore it has many applications in the food and pharmaceutical industry – e.g. as solvent or as preservative in food and pet food products. Further uses are in the de-/anti-icing as well as the lubricant sectors.

68.4 Systems characterization

In the production process for propylene glycol the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of propylene glycol is not considered to be high.

For this inventory the functional unit is 1 kg propylene glycol. As process location Europe (RER) was used. The process chain was assessed as shown in the following figure.

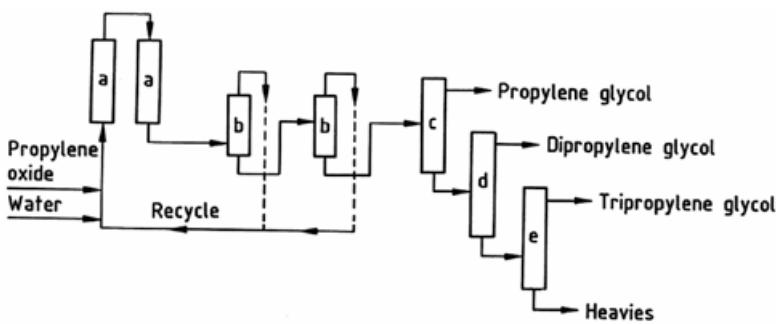


Fig. 68.1 Process chain for the production of propylene glycol (Fig. 5 out of Sullivan (2000) - showing reactor [a], evaporator [b] and the different distillation [c] - [e])

68.5 Propylene glycol, at plant (Location: RER)

68.5.1 Process

This dataset includes a rough estimation of the production process for propylene glycol. Due to missing production data this inventory bases on stoichiometric calculations. For these calculations a process yield of 95% for the used chemicals was assumed (Wells (1991)). The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in an internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

According to Sullivan (2000) propylene oxide and water are combined in the initial stage of the process at a molar rate of 1:1 at a temperature of 125° and a pressure of about 2 MPa. As this is an exothermic reaction the effluent from the reactor has a temperature of 190°C. With the mentioned ratio, the result of propylene glycol, dipropylene glycol and tripropylene glycol is about 100 : 10 : 1. As propylene glycol is more than 90%, the production of the two other substances is not further considered within this study. Also the catalysts used for the reaction were omitted due to missing data on the amounts used. It was assumed that they do not have an important contribution on the final result of the inventory. The overall reaction for the production of propylene glycol can be formulated as follows:



68.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the waste water treatment. Fossil fuel is needed to generate the desired heat for the preheating and the distillation of the product. There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the propylene glycol production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was used. A summary of the values used is given in Tab. 68.2.

Raw materials and Chemicals

For the production of 1 kg propylene glycol the following stoichiometric inputs are needed (yield 100%):

- Propylene oxide, $\text{CH}_2\text{OC}(\text{CH}_3)\text{H}$: 763.2 g (13.2 mol)
- Water, H_2O : 236.8 g (13.2 mol)

For the production a yield of 95% was used as given in (Wells (1991)). To produce 1 kg propylene glycol therefore 803.3 g propylene oxide and 249.3 g water are considered as raw materials in this inventory. A summary of the values used is given in Tab. 68.2.

Water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the propylene glycol production. According to the ongoing IPPC research of the European Commission the cooling water demand may reach 86 kg kWh^{-1} for an once through cooling system, which would lead to a cooling water demand of 48 kg per kg product for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m^3 cooling water per kg product was used.

Transport

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2007) are used for the different raw materials.

68.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg propylene glycol is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of propylene glycol. As approximation the air emissions occurring from the purge vent, the distillation vent and fugitive emission sources were estimated to 0.2% of the raw material input.

This assumption leads to air emissions of 1.6 g propylene oxide per kg product.

Emissions to water

The remaining amount of un-reacted raw materials was assumed to leave the production process with the waste water. This assumption leads to a pollution of the waste water with 38.5 g propylene oxide per kg product. Further it was assumed that this waste water is treated in an internal waste water plant. The removal efficiency for propylene oxide was assumed with 90% leading to emissions of 3.85 g propylene oxide per kg product in the treated water. The carbon contained in the removed propylene oxide was accounted as CO_2 emissions to air (78.75 g CO_2 per kg product). The values for COD,

BOD, TOC and DOC used in this inventory were calculated from the amount of propylene oxide in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 68.2.

Solid wastes

Solid wastes occurring during the production of propylene glycol e.g. spent catalysts were neglected in this inventory.

Tab. 68.2 Energy demand, Resource demand and emissions for the production of propylene glycol.

[per kg propylene glycol]			Remark
INPUTS			
propylene oxide	kg	0.803	stoichiometric calc., 95% yield
Water, unspecified	m3	2.49E-04	stoichiometric calc., 95% yield
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m3	2.40E-02	estimation
Transport, by train	tkm	4.82E-01	standard distances & means
Transport, by lorry	tkm	8.03E-02	standard distances & means
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
propylene oxide, to air	kg	1.60E-03	estimated as 0.2% of input
carbon dioxide, fossil, to air	kg	7.88E-02	from waste water treatment
propylene oxide, to water	kg	3.85E-03	calculated from mass balance
COD, BOD	kg	5.91E-02	calculated from water emissions
TOC, DOC	kg	1.85E-02	calculated from water emissions

68.5.4 Infrastructure

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg propylene glycol was included.

68.6 Data quality considerations

The following figure shows the data quality indicators for the inventory of propylene glycol production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the propylene glycol production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data.

Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 68.9.

Tab. 68.3 Input / Output and uncertainty for the process “propylene glycol, at plant (RER)”

Explanation	Name	Location	Unit	propylene glycol, liquid, at plant		uncertaintyType	standardDeviation95%	GeneralComment
				RER	o			
				kg	kg			
Resource Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant	
	Water, unspecified natural origin		m3	2.49E-04	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	propylene oxide, liquid, at plant	RER	kg	8.03E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant	
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5.5,1,1,4,5); estimated with data from a large chem. plant	
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation	
	transport, freight, rail	RER	tkm	4.82E-01	1	2.09	(4,5,na,na,na,na); standard distances	
	transport, lorry 32t	RER	tkm	8.03E-02	1	2.09	(4,5,na,na,na,na); standard distances	
	propylene glycol, liquid, at plant	RER	kg	1				
	Heat, waste		MJ	1.20E+00	1	1.88	(5.5,1,1,4,5); calculated from electricity input	
Output Air emission Water emission	Carbon dioxide, fossil		kg	7.88E-02	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	Propylene oxide		kg	1.60E-03	1	2.32	(5,5,na,na,na,5); estimation	
	BOD5, Biological Oxygen Demand		kg	5.91E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	COD, Chemical Oxygen Demand		kg	5.91E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	DOC, Dissolved Organic Carbon		kg	1.85E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	TOC, Total Organic Carbon		kg	1.85E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	Propylene oxide		kg	3.85E-03	1	3.55	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	

68.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

68.8 Conclusions

The inventory for propylene glycol is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if propylene glycol is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

68.9 EcoSpold Meta Information

ReferenceFunction	Name	propylene glycol, liquid, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Propylenglykol, flüssig, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid propylene glycol. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	57-55-6
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from propylene oxide and water with a process yield of 95%. Inventory bases on stoichiometric calculations. The emissions to air (0.2 wt.% of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

68.10 References

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69 Propylene oxide

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69.1 Introduction

Propylene oxide ($\text{HOCH}_2\text{OC}(\text{CH}_3)\text{H}$, CAS-No. 75-56-9) is a very reactive substance and one of the most important chemical intermediates (Kahlich et al. (2000)). At room temperature it is colourless, low-boiling liquid with a sweet odour. For this inventory the functional unit is 1 kg liquid propylene glycol. The most important chemical and physical properties of propylene oxide used in this inventory are given here.

Synonyms for propylene oxide: 1,2-epoxypropane, methyloxirane

Tab. 69.1 Chemical and physical properties of propylene oxide

Property	Unit	Value	Remarks
Molecular weight	58.08	g mol^{-1}	
Vapour pressure	58.8	KPa	at 20 °C
Boiling point	34.23	°C	at normal pressure
Melting point	-111.93	°C	at normal pressure

69.2 Reserves and Resources of material

The annual worldwide production capacity at the beginning of the 90s was around 4 Mt. Nowadays, this substance is produced in big production sites with capacities of 100'000 t/a and more. Therefore, the two companies Dow and Arco are responsible for more than 80% of the annual propylene oxide production.

For the production of propylene oxide several different production ways are possible (see Kahlich et al. (2000)). From all of them, only two ways actually are exploited industrially – the chlorohydrin and the indirect oxidation processes. Another method used so far, was the direct gas-phase oxidation with silver catalysts. In all cases, the process produces not only the desired propylene oxide, but also considerably amounts of co-products. According to Kahlich et al. (2000), the production capacities in 1996 were about half (49%) from chlorohydrin process and about a quarter from the styrene process as well as from the tert-butyl alcohol process. In this inventory, only the production of propylene oxide with the chlorohydrin process is further investigated.

69.3 Use of material / product

According to Kahlich et al. (2000), propylene oxide got in the last 50 years one of the most important intermediates chemicals. Today, this chemical is used for a broad spectrum of products, e.g. polymers (polyurethanes, polyesters), oxygenated solvents (propylene glycol ethers) or industrial fluids (polyglycols). A distribution to the most important applications / derivatives shows about the following picture: 51% for flexible foams, 22% for propylene glycol, 10% for rigid foams.

69.4 Systems characterization

In the production process for propylene oxide the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents

therefore only a rough estimation of the process requirements and should be used only for processes where the impact of propylene oxide is not considered to be high.

For this inventory the functional unit is 1 kg propylene oxide. As process location Europe (RER) was used. The process was assessed according to the different steps in the following figure.

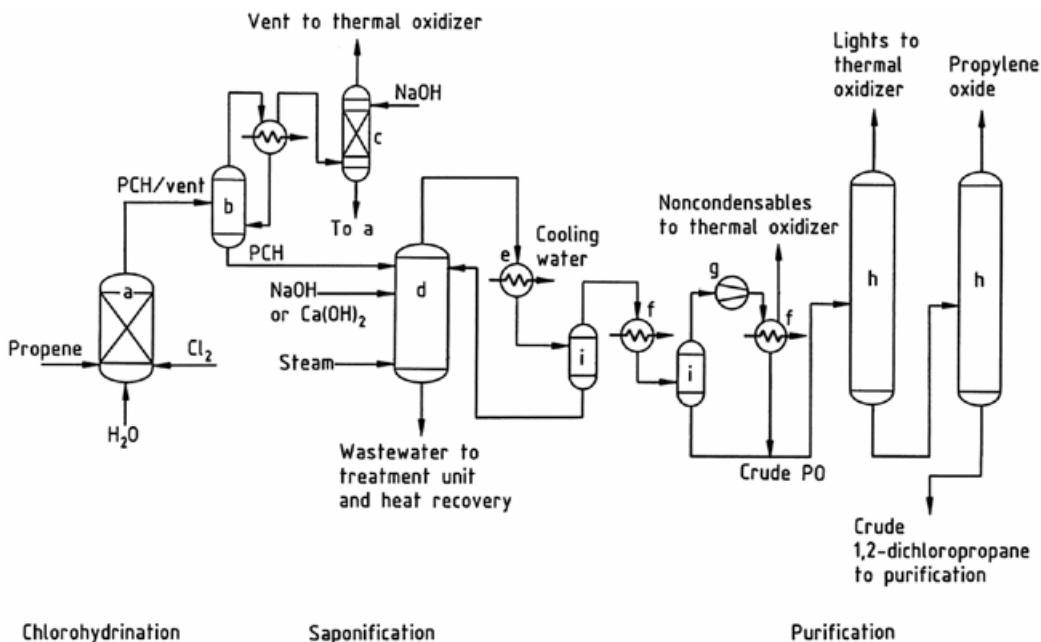


Fig. 69.1 typical arrangement for the production of propylene oxide (Fig. 4 out of Kahlich et al. (2000))

69.5 Propylene oxide, at plant (Location: RER)

69.5.1 Process

This dataset includes a rough estimation of the production process for propylene oxide with the chlorohydrin process. Due to missing production data this inventory bases on information given in Kahlich et al. (2000). The emissions to air and water were estimated using mass balance. It was assumed that waste water is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The overall reaction for the production of propylene oxide by the chlorohydrin process can be formulated as follows:



According to Kahlich et al. (2000), the commercial chlorohydrin process consists of two steps: (i) the synthesis of propylene chlorohydrin, and (ii) the dehydrochlorination of propylene chlorohydrin to propylene oxide with the aid of a base, usually either lime or sodium hydroxide. In a final step, the product is purified while the waste water are treated in a internal waste water treatment plant.

For this study, sodium hydroxide is used as the only base material used within the process, although Kahlich et al. (2000) shows that about half of the European chlorohydrin processes us lime.

Actually, a commercial production line uses gaseous propene and gaseous chlorine about in a equimolar relation within an excess of water, resulting in a diluted solution of propylene chlorohydrin, HCl

and minor amounts of further chlorinated hydrocarbons by-products. An example for the unit ratios of the propylene oxide is shown in Fig. 69.2.

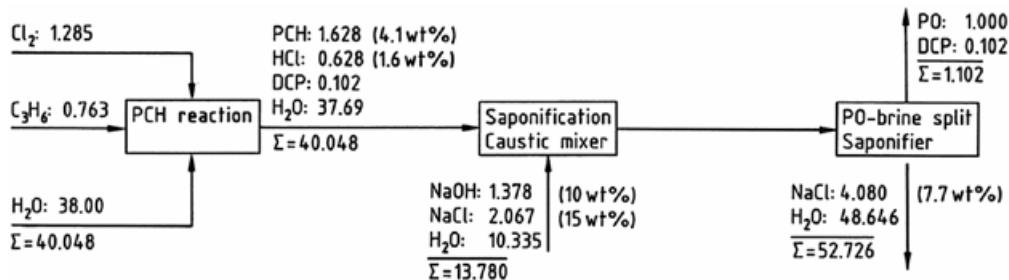


Fig. 69.2 Unit ratios of the propylene oxide production within the chlorohydrin process (Fig. 5 out of Kahlich et al. (2000), based on an assumed water - propene ratio of 50:1 and caustic soda as cell liquor)

69.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the waste water treatment. Fossil fuel is needed to generate the desired heat within the process scheme. There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the propylene oxide production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used. A summary of the values used is given in Tab. 69.2.

Raw materials and Chemicals

For the production of 1 kg propylene oxide, the amounts for propene, chlorine and the base according to the information shown above in Fig. 69.2 are used within this study. A summary of the values used is given in Tab. 69.2.

Cooling water use

There was no information available on the amount of cooling water used within the plant. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the propylene oxide production. According to the ongoing IPPC activities of the European Commission, the cooling water demand may reach 86 kg kWh^{-1} for a once through cooling system, which would lead to a cooling water demand of 48 kg per kg product for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m^3 cooling water per kg product was used.

Transport

According to Kahlich et al. (2000), the production process with sodium hydroxide as base is used in plants where chlorine is originating from mercury or membrane processes. Therefore, for this study it is assumed that those two input materials are transported by pipeline systems from the chlorine electrolysis cell to the propylene oxide plant. For the other input materials, standard distances and means according to Frischknecht et al. (2007) are used.

69.5.3 Emissions

Waste heat

It was assumed that 100% of the electricity consumed, i.e. 1.2 MJ per kg propylene oxide, is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of propylene oxide. According to Kahlich et al. (2000), the reactor vent gas is a mixture of excess propene or chlorine and further reaction products. For this study, as an approximation the air emissions occurring from the reactor vent are estimated to 0.2% of the mentioned raw material inputs.

This assumption leads to air emissions of 1.53 g of propene and 2.57 g of chlorine per kg product.

Emissions to water

The remaining amount of unreacted raw materials was assumed to leave the production process with the wastewater. This assumption leads to a pollution of the waste water with 1.282 kg chlorine, 36.97 g propene per kg product and the base - here 1.378 kg NaOH. Further it was assumed that this wastewater is treated in an internal wastewater plant. Therefore, a removal efficiency of 90% for propene was assumed, leading to 3.70 g propene in the treated water. The carbon contained in the removed propene was accounted as CO₂ emissions to air (0.104 kg CO₂ per kg product). According to the above shown reaction scheme chlorine is in form of hydrogen chloride (HCl) in the wastewater. It was assumed in this study that HCl and NaOH are neutralized within the waste water treatment plant, leading to emissions of 2.565 kg Cl⁻ and 0.792 kg Na⁺ in the leaving water. The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amount of propene in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 69.2.

Solid wastes

Solid wastes occurring during the production of propylene oxide were neglected in this inventory.

Tab. 69.2 Energy demand, resource demand and emissions for the production of propylene oxide.

[per kg propylene oxide]			Remark
INPUTS			
chlorine	kg	1.285	data from Kahlich et al. 2000
propene	kg	0.763	data from Kahlich et al. 2000
sodium hydroxide	kg	1.378	data from Kahlich et al. 2000
Water, unspecified	m3	3.80E-02	data from Kahlich et al. 2000
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
Water, cooling, unspecified	m3	2.40E-02	estimation
Transport, by train	tkm	4.58E-01	standard distances & means
Transport, by lorry	tkm	7.63E-02	standard distances & means
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
propene, to air	kg	1.53E-03	estimated as 0.2% of input
chlorine, to air	kg	2.57E-03	estimated as 0.2% of input
carbon dioxide, fossil, to air	kg	1.04E-01	from waste water treatment
propene, to water	kg	3.70E-03	calculated from mass balance
chloride, to water	kg	2.57E+00	calculated from mass balance
sodium, to water	kg	7.92E-01	calculated from mass balance
COD, BOD	kg	1.21E-01	calculated from water emissions
TOC, DOC	kg	3.17E-02	calculated from water emissions

69.5.4 Infrastructure

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg propylene glycol was included.

69.6 Data quality considerations

The following table shows the data quality indicators for the inventory of propylene oxide production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the propylene oxide production has a high uncertainty, because only few data of the production processes were available. Therefore the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 69.9.

Tab. 69.3 In- / Outputs and uncertainty information for the module “propylene oxide, at plant”

Explanation	Name	Location	Unit	propylene oxide, liquid, at plant		uncertaintyType standardDeviation95%	GeneralComment
				RER	o kg		
	Infrastructure	Process	Unit				
Resource	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
Input from Technosphere	Water, unspecified natural origin		m3	3.80E-02	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	1.38E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	propylene, at plant	RER	kg	7.63E-01	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	chlorine, liquid, production mix, at plant	RER	kg	1.29E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 90-99.8%
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation
	transport, freight, rail	RER	tkm	4.58E-01	1	2.09	(4,5,na,na,na,na); standard distances
	transport, lorry 32t	RER	tkm	7.63E-02	1	2.09	(4,5,na,na,na,na); standard distances
Output	propylene oxide, liquid, at plant	RER	kg	1			
Air emission	Heat, waste	MU	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input	
	Carbon dioxide, fossil	kg	1.04E-01	1	1.88	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	Chlorine	kg	2.57E-03	1	2.32	(5,5,na,na,na,5); estimation	
	Propene	kg	1.53E-03	1	2.32	(5,5,na,na,na,5); estimation	
Water emission	BOD ₅ , Biological Oxygen Demand	kg	1.21E-01	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	COD, Chemical Oxygen Demand	kg	1.21E-01	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	DOC, Dissolved Organic Carbon	kg	3.17E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	TOC, Total Organic Carbon	kg	3.17E-02	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	Chloride	kg	2.57E+00	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	Sodium, ion	kg	7.92E-01	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	
	Propene	kg	3.70E-03	1	2.11	(5,5,na,na,4,5); estimated from mass balance and WWTP effic.	

69.7 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

69.8 Conclusions

The inventory for propylene oxide is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if propylene oxide is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

69.9 EcoSpold Meta Information

ReferenceFunction	Name	propylene oxide, liquid, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Propylenoxid, flüssig, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid propylene oxide. Quite large uncertainty of the process data due to missing data on process emissions.
ReferenceFunction	CASNumber	75-56-9
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from propene and chlorine, using the chlorohydrin process and an estimated process yield of 90-95%. Inventory bases on one single literature source. The emissions to air (0.2 wt. % of raw material input) and water were estimated using mass balance. Treatment of the waste water in a internal waste water treatment plant assumed (elimination efficiency of 90% for C).
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	Process data based on few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

69.10 References

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70 Rare earth oxide production from bastnasite

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Last changes:

10.12.2007

70.1 Introduction

Rare earths are not actually rare, but they are found in differing degrees of abundance. The more abundant cerium and lanthanum are as common as copper, whereas others, such as europium or terbium, are not particularly abundant. This leads to supply differences, and, when coupled with different demand characteristics, to differences in price. Rare earths have unique properties that make them indispensable for many technological applications. They consequently play a critical role in the electronics, automotive, environmental protection and petrochemical sectors (Sinton, 2006).

70.2 Characterisation of material product

The rare earths are a group of metallic elements consisting of the lanthanide series on the periodic table as well as yttrium. They can be subdivided into the light or ceric elements (Ce, La, Nd, Pr) and the heavy or yttric elements (Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu). This grouping comes about from the similarity in their chemical behaviour which, in turn, results in their intimate occurrence in natural deposits (Sinton, 2006). Tab. 70.1 shows the physical properties of the rare earth oxides (REO) investigated in this inventory.

Tab. 70.1 Properties of rare earth oxides and rare earth elements

Rare earth oxide	Formula	Molecular weight g/mol	Specific gravity g/cm ³	Melting point °C	Value *) US\$/kg	Rare earth element	Symbol	Molecular weight g/mol
Cerium oxide	CeO ₂	172.12	7.3	2600	1.5	Cerium	Ce	140.12
Lanthanum oxide	La ₂ O ₃	325.81	6.6	2305	1.75	Lanthanum	La	138.91
Neodymium oxide	Nd ₂ O ₃	336.48	7.3	2320	8.9	Neodymium	Nd	144.24
Praseodymium oxide	Pr ₆ O ₁₁	1021.44	6.9	2200	9.6	Praseodymium	Pr	140.91
Europium oxide	Eu ₂ O ₃	351.92	7.3	2350	270	Europium	Eu	151.96
Gadolinium oxide	Gd ₂ O ₃	362.50	7.6	2420	49 **)	Gadolinium	Gd	157.25
Samarium oxide	Sm ₂ O ₃	348.72	7.1	2335	2.5	Samarium	Sm	150.36

*) Average rare earth oxide bulk prices FOB China, 9.2004 - 9.2006, min. 99% purity (Lynas, 2006b)

**) Not available; price for dysprosium oxide; according to Hedrick (2004) similar prices for Gd₂O₃ and Dy₂O₃

Tab. 70.2 shows the composition of the rare earth ore concentrates and oxides investigated in this inventory.

Cerium, the second element in the lanthanide series, is the most abundant. Cerium oxide is a light yellowish powder. It is mainly used for glass colouring and as a glass polishing powder.

Lanthanum oxide is a white powder used as raw material for optical glass, optical fibres and catalysts.

Neodymium oxide is a light purple powder. It is mainly used for colouring glass and ceramics, but also as a raw material for magnets.

Praseodymium oxide is a black or black-brown powder. It is used as a raw material for high-quality yellow pigments in ceramics.

Samarium-europium-gadolinium concentrate is an intermediate product and is separated into individual rare earth products in further process steps, which are not investigated in this inventory.

Tab. 70.2 Composition of rare earth oxides investigated in this inventory

Product	TREO *) %	Purity % of TREO	REO Composition % of TREO
Rare earth concentrate from bastnasite	70% REO **)	70% REO	49% CeO ₂ , 28% La ₂ O ₃ , 15.4% Nd ₂ O ₃ , 5.1% Pr ₆ O ₁₁ , 1.2% Sm ₂ O ₃ , 0.23% Eu ₂ O ₃ , 0.58% Gd ₂ O ₃
Cerium concentrate	98% REO	60% CeO ₂	Min. 60% CeO ₂ , max. 20% La ₂ O ₃ , max. 1% Nd ₂ O ₃
Lanthanum oxide	99% REO	99.95% La ₂ O ₃	Max. 0.03% CeO ₂ , 0.005% Nd ₂ O ₃ , 0.005% Pr ₆ O ₁₁
Neodymium oxide	99% REO	99.5% Nd ₂ O ₃	Max. 0.03% CeO ₂ , 0.03% La ₂ O ₃ , 0.4% Pr ₆ O ₁₁
Praseodymium oxide	99% REO	99% Pr ₆ O ₁₁	Max. 0.03% CeO ₂ , 0.03% La ₂ O ₃ , 0.5% Nd ₂ O ₃
Samarium europium gadolinium concentrate	94% REO	94% REO	Min. 50% Sm ₂ O ₃ , 8.5% Eu ₂ O ₃ , 14% Gd ₂ O ₃ Max. 1% CeO ₂

*) Total Rare Earth Oxide (TREO); Difference to 100% are impurities such as CaO, SiO₂, Fe₂O₃, etc.
**) For detailed composition, see Tab. 70.3
Source: HeFa (2006) or calculated from ore composition; Values as wt.-%

70.3 Reserves and resources of material

Bastnasite (RE)CO₃F is the most important source of light rare earth oxides (REO) such as cerium and lanthanum. It is a fluorocarbonate of the cerium group of rare earth metals and contains almost no thorium. The rare earth oxide content of bastnasite is typically 60% (Molycorp, 1993). Leached bastnasite concentrate reaches a content of 68-73 percent REO (Molycorp, 2006). The rare earth content of bastnasite concentrate contains as much as 99% of light rare earths (La-Nd), almost no heavy rare earths, and very little yttrium. Tab. 70.3 shows the composition of saleable rare earth ore concentrate and Tab. 70.4 that of various ores of individual rare earth oxides.

A typical rare earth ore consists of about 10 – 12 weight percent bastnasite, 40 percent calcite (and/or dolomite), 25 percent barite and celestite and further strontianite, quartzite, magnetite and fluorite (Valdiviezo & Lins 1997). The ore mined in Baotou (China) also contains magnetite and hematite (instead of barite) and is therefore also used for iron mining. Bastnasite can be more easily decomposed than most silicate or phosphate minerals.

Another resource for rare earth oxides is the mineral monazite. It is a phosphate containing rare earths mainly of the cerium group as well as thorium. The primary monazite deposits have been useful sources of as rare earths in a few instances.

Tab. 70.3 Composition of various ore concentrates of rare earth oxides

Ore Composition (in wt.-%)	Typical concentrate 60% REO	Molycorp, concentrate, leached	Baotou, concentrate (China)	Baiyunebo, concentrate (China)	Stoechiometric	Used in this Study
Rare earth oxides (REO)	60.0%	68.0 - 73.0%	66.3-70.7%	68.4%	74.76%	70.0%
Strontium oxide: SrO	5.0%	1.0%	0.06-1.1%	-	0.00%	1.0%
Calcium oxide: CaO	4.0%	1.8%	-	3.6%	0.00%	1.0%
Barium oxide: BaO	1.5%	2.7%	0.3-5.4%	0.11%	0.00%	1.0%
Fluorine: F	5.5%	-	6.4-9.8%	8.6%	8.72%	8.0%
Silica oxide: SiO ₂	1.5%	2.5%	0.11-1.1%	0.45%	0.00%	0.4%
Iron oxide: Fe ₂ O ₃	0.5%	0.6%	0.25-0.84%	0.80%	0.00%	0.5%
Phosphorus pentoxide P ₂ O ₅	1.0%	1.2%	-	1.9%	0.00%	1.0%
Magnesium oxide: MgO	-	-	0.68-3.04%	-	0.00%	0.4%
Thorium oxide: ThO ₂	-	-	0.02-1.34%	0.14%	0.00%	0.1%
Loss on ignition: CO ₂	20.0%	20.0%	16.2-22.1%	-	20.20%	20.0%
-O = F2 (Balance for O ₂)	-	-	-3.1..-4.1%	N.A.	-3.67%	-3.4%
Source	Molycorp, 1993	Molycorp, 2006	Peishan et al., 1995	Wenli et al., 2000	calculated	

Tab. 70.4 Rare earth oxide composition of various ores

Mine Rare earth oxide	Formula	Mountain Pass CA, bastnasite	Baotou, China, bastnasite	Mt. Weld, Australia, monazite	Used in this Study	composition as rare earth metal
Cerium	CeO ₂	49.10%	50.80%	46.74%	49.13%	Ce 40.00%
Dysprosium	Dy ₂ O ₃	trace	0.10%	0.12%	0.00%	Dy 0.00%
Erbium	Er ₂ O ₃	trace	trace	trace	0.00%	Er 0.00%
Europium	Eu ₂ O ₃	0.10%	0.21%	0.44%	0.23%	Eu 0.10%
Gadolinium	Gd ₂ O ₃	0.20%	0.60%	0.75%	0.58%	Gd 0.25%
Holmium	Ho ₂ O ₃	trace	trace	trace	0.00%	Ho 0.00%
Lanthanum	La ₂ O ₃	33.20%	26.50%	25.50%	28.15%	La 12.00%
Lutetium	Lu ₂ O ₃	trace	trace	trace	0.00%	Lu 0.00%
Neodymium	Nd ₂ O ₃	12.00%	15.40%	18.50%	15.40%	Nd 6.60%
Praseodymium	Pr ₆ O ₁₁	4.34%	4.96%	5.32%	5.07%	Pr 0.70%
Samarium	Sm ₂ O ₃	0.80%	1.10%	2.27%	1.16%	Sm 0.50%
Terbium	Tb ₄ O ₇	trace	0.03%	0.05%	0.00%	Tb 0.00%
Thulium	Tm ₂ O ₃	trace	trace	trace	0.00%	Tm 0.00%
Ytterbium	Yb ₂ O ₃	trace	trace	trace	0.00%	Yb 0.00%
Yttrium	Y ₂ O ₃	0.10%	0.20%	0.25%	0.00%	Y 0.00%
Not accounted (Difference to 100% REO)		0.16%	0.10%	0.06%	0.28%	
REO content in ore		8.5%	5.0%	15.0%	6.00%	in ore 3.61%

Bastnasite is a primary source of light REO in the enormous deposits of Bayan Obo in China (800 million metric tons of ore; 5-6% REO) and at Mountain Pass, California, USA (3.3 million metric tons; 7-8% REO). Bastnasite is the most important mineral source of rare earth oxide production with 77% of rare earth resources worldwide. China is the country with the largest reserves of rare earths (Gupta & Krishnamurthy, 2005). Besides the deposits in Bayan Obo, the monazite rare earth deposit in Mount Weld, Western Australia, ranks as one of the richest major rare earth resources in the world with 5.4 million metric tons of REO. This monazite deposit is also low in the radioactive element thorium (Gupta & Krishnamurthy 2005, Patersons 2006).

By 2002, more than 80% of all REO produced was from bastnasite, about 10% from ion adsorption ores, 5% from monazite and the remainder from other sources (Gupta & Krishnamurthy, 2005). In this inventory, the production of rare earth oxides was investigated only for bastnasite.

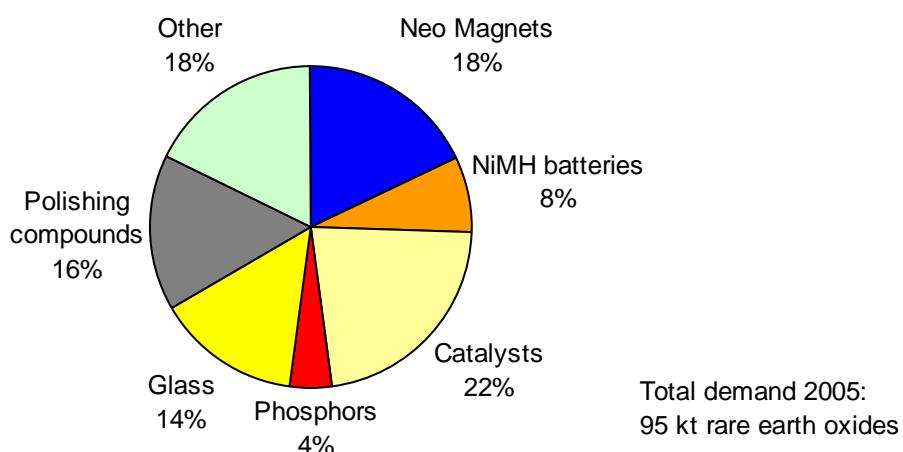
Tab. 70.5 Production and resources of rare earth oxides and elements

Country	Mine Production 2005		Published Reserves	
	t REO	%	t REO	%
China *)	98'000	93.3%	43'000'000	42.7%
United States	N.A.	N.A.	13'000'000	12.9%
India	2'700	2.6%	1'100'000	1.1%
Australia	N.A.	N.A.	5'200'000	5.2%
Brazil	N.A.	N.A.	109'000	0.1%
Russia and CIS	N.A.	N.A.	19'000'000	18.9%
Canada	N.A.	N.A.	940'000	0.9%
South Africa	N.A.	N.A.	390'000	0.4%
Malaysia	250	0.2%	30'000	0.0%
Vietnam	N.A.	N.A.	9'000'000	8.9%
Thailand	2'200	N.A.	N.A.	N.A.
Other countries	1'850	1.8%	9'000'000	8.9%
Total	105'000	100.0%	100'769'000	100.0%

Sources: Sinton 2006, Hendrick 2006
*) In Hendrick (2006) the Reserves in China are accounted only with 27 Mt

70.4 Use / application of product

Fig. 70.1 shows the share of rare earth oxide demand (2005) for the most important applications. The use of rare earths for permanent magnets, consumer electronics and automotive catalytic converters is expected to grow. In particular, growth in demand will be seen in the automotive industry as electric components increasingly replace hydraulic systems and NiMH rechargeable batteries are used in hybrids. The growth in energy-efficient lighting and flat screen displays will boost the growth of rare earth phosphors²⁴ over the next five years (Sinton, 2005).

**Fig. 70.1 Rare earth demand by applications in 2005 (Sinton, 2006)**

²⁴ Europium, terbium and dysprosium are used for fluorescent lighting

Eighty percent of polishing compounds are produced as standard polishing powders and 20% as high-purity polishing powders. Polishing powders normally contain cerium oxide (an average of 68% of total REO), lanthanum oxide (24% of total REO) and praseodymium oxide (8% of total REO).

Phosphors are chemical compounds that emit light under certain conditions. They are used in the production of LCD flat panel displays (televisions and computer monitors) and in energy-efficient lighting. Europium is an important compound for the production of red phosphor.

The demand for rare earths in other applications includes metallurgy, fertilizers (China), advanced ceramics, lighter flint mischmetal, lasers, water treatment and pharmaceuticals.

Fig. 70.2 shows the share of individual rare earth oxides in total demand in 2005. A strong rise in demand is expected in future for lanthanum for NiMH batteries, neodymium, praseodymium, dysprosium and terbium, as these elements are used in neo magnets, and europium due to the growth in phosphors. Rare earth markets will require higher purity mixed and separated rare earth products to meet this growing demand (Sinton, 2005).

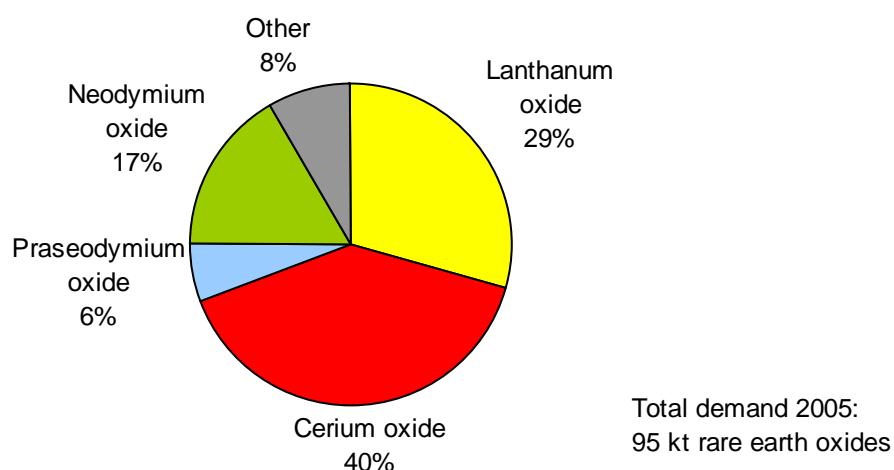


Fig. 70.2 Rare earth oxide demand in 2005 (Sinton, 2006)

70.5 System characterisation

The process of mining and beneficiating rare earth oxides consists of the following steps:

- Mining of bastnasite
- Mineral concentration by froth flotation. Product: Rare earths concentrate
- “Cracking” of minerals and extraction of rare earths into concentrate subgroups. Separation of individual rare earths by solvent extraction

At Bayan Obo (China), the main ore body has an average REO content of 6.19%, the east ore body 5.17%, and the west ore body approximately 1%. Fluorine occurrence is widespread in the mine but more than 98% of the fluorine in the deposits occurs primarily as fluorite and as a minor component in bastnasite (Gupta & Krishnamurthy, 2005). Bastnasite-bearing carbonatite comes from Mianning in Sichuan Province (about 40% of Chinese rare earth production). An average REO concentration of 6% in the crude ore and a bastnasite content of 10% of the crude ore is used.

Much of the world's rare earth production comes from its recovery as a by-product of iron ore mining at Bayan Obo, China. The crude bastnasite has a rare earth content of about 11% REO after physical

beneficiation and separation from the magnetic ores. This co-production is not included but this fact is considered in the average REO concentration of 6% in the ore (e.g. concentration from 1% to 6% REO in the west ore body of Bayan Obo allocated to iron mining).

The most important rare earth deposits in hard rock are mined as open-pit operations by drilling, blasting, loading and hauling to the mill. To recover the bastnasite concentrate from crude ore, steam is used to condition the ore before flotation. The flotation concentrate, which contains 60% REO, is leached with 10% hydrochloric acid to remove calcite and obtain a rare earth concentrate with 70% REO (Gupta & Krishnamurthy, 2005).

Various process routes may be used for cracking and separating individual rare earths from the concentrate. They are described in Gupta & Krishnamurthy (2005). Only the process used in China to crack Baotou bastnasite is investigated for this inventory. This process relies on roasting the concentrate with concentrated sulphuric acid at temperatures of around 500°C to remove fluoride and carbon dioxide. Further purification processes are often performed in a chloride solution. Nitric solutions are also used in some processes. A process using a chloride rare earth solution is investigated.

The mixtures derived from mineral cracking can be further processed to separate individual elements. Because of the generally similar chemical properties of the rare earths, their separation can be time-consuming and expensive. Solvent extraction (SX) is used for the initial stage of separation and results in materials of up to 99.9% purity (Sinton, 2006).

There are many advantages of using solvent extraction in rare earth separation. One of them is that the rare earth loading in the solvent/extractant can be very high (~180 g REO per litre). Aqueous solutions with concentrations of 100-140 g REO per litre can therefore be used. This results in compact equipment, an important factor due to the large number of separation stages needed for this process (Gupta & Krishnamurthy, 2005).

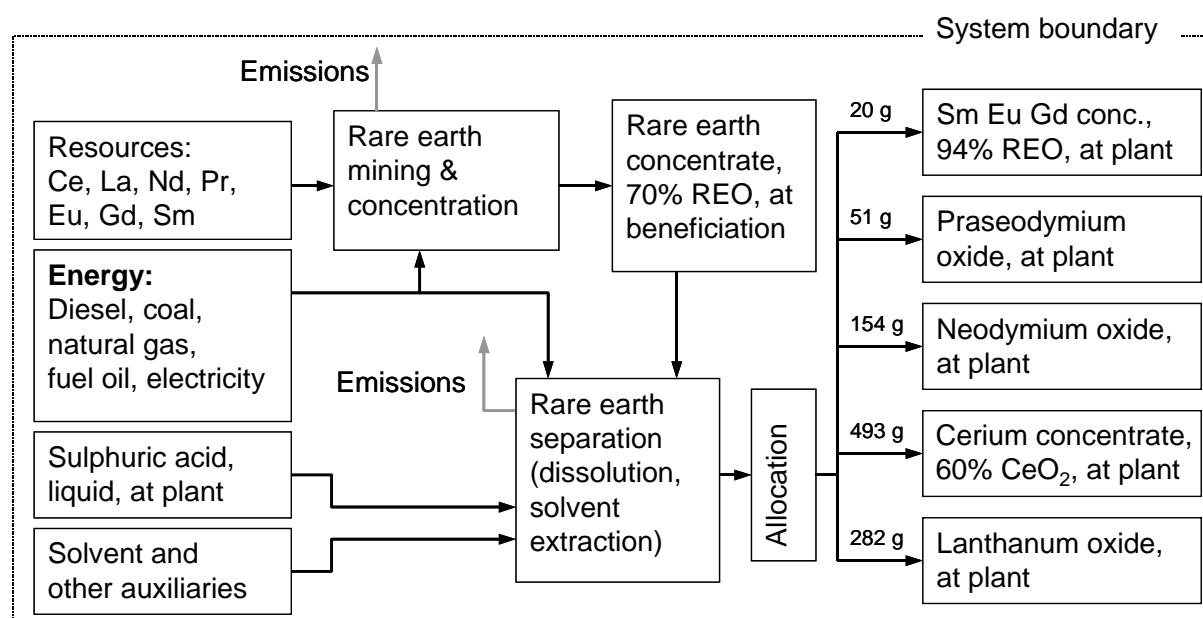


Fig. 70.3 System outline of rare earth oxide production from bastnasite

70.6 Rare earth concentrate from bastnasite, at mine

70.6.1 Process

Bastnasite is mined from open pit mines. The ore from these mines is usually removed by blasting and use of power shovels. Mining is carried out with large haulage trucks and front-end loaders. The crude ore is screened and scrubbed in order to remove oversize material,²⁵ which is returned to the mining pit. The mined product is fed to a flotation process, thickened, filtered, and dried in a rotary kiln to produce a rare earth oxide (REO) concentrate. The concentrate is further upgraded to 70% REO by leaching with 10% hydrochloric acid to remove calcite. A simplified process scheme for rare earth concentrate production from bastnasite is shown in Fig. 70.4.

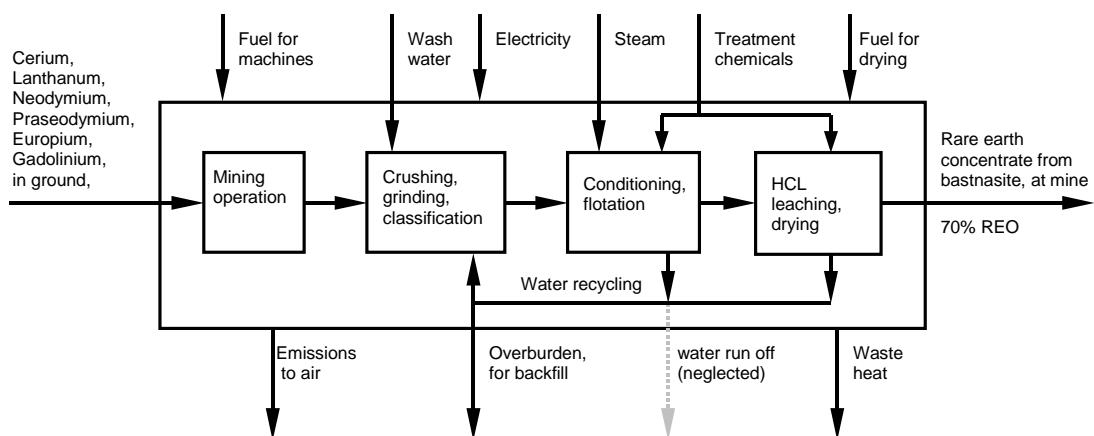


Fig. 70.4 Simplified process flowchart of rare earth concentrate production from bastnasite

70.6.2 Resources

A rare earth concentration (REO) in the crude ore of 6 percent is used. A recovery rate of 50 to 70 percent is reached for the concentration and beneficiation process (Lynas 2006a, Patersons 2006, Gupta & Krishnamurthy 2005). A yield of 60 percent is used. In order to produce 1 kg of rare earth concentrate from bastnasite with a rare earth oxide (REO) concentration of 70%, 19.44 kg of crude ore is needed. On the basis of a crude ore concentration of 6% REO (equals 3.61% rare earth metal content in the crude ore), a bastnasite content of 10% in the crude ore and the ore composition given in Tab. 70.4, the following ground resources are needed:

- Cerium, 24% in bastnasite, 2.4% in crude ore, in ground: 467 g
- Lanthanum, 7.2% in bastnasite, 0.72% in crude ore, in ground: 140 g
- Neodymium, 4% in bastnasite, 0.4% in crude ore, in ground: 77 g
- Praseodymium, 0.42% in bastnasite, 0.042% in crude ore, in ground: 8.17 g
- Europium, 0.06% in bastnasite, 0.006% in crude ore, in ground: 1.17 g
- Samarium, 0.3% in bastnasite, 0.03% in crude ore, in ground: 5.83 g
- Gadolinium, 0.15% in bastnasite, 0.015% in crude ore, in ground: 2.92 g

²⁵ Oversize material can consist of rocks, clay, organic matter and other debris

The overburden, topsoil and waste rock are neglected as resources in this inventory because they are back-filled into the mine and used for land reclamation.

70.6.3 Energy use and auxiliaries

Process energy use for mining

No detailed information is available on the energy consumption of the various mining operations. These are calculated with data from Kippenberger (1999) for phosphate rock mining based on the mass of crude ore material moved. This leads to an energy requirement of 0.057 kWh electricity and 0.1 MJ diesel per kg of rare earth concentrate with 70% REO (6% REO in crude ore, 60% recovery rate: 19.44 kg crude ore per kg rare earth concentrate).

The energy requirement (diesel and electricity) for mining operations used here is similar to the values presented in Classen et al. (2007) for iron, copper (0.11 MJ per kg crude ore) and bauxite mining (0.21 MJ per kg crude ore).

Process energy use for beneficiation

According to Cohen (2005), the electricity requirement for mineral sorting operations ranges from 0.2 to 3.0 kWh/t of feed material. Classen et al. (2007) use a value of 0.004 kWh per kg crude ore for iron ore beneficiation and 0.017 kWh per kg crude ore for copper ore beneficiation. For phosphate rock beneficiation, an electricity requirement of 0.016 kWh per kg crude ore for washing and flotation and a heat requirement of 0.058 MJ per kg crude ore are calculated from the data of Patyk & Reinhardt (1997). It is assumed that the process operation for rare earth beneficiation is closer to that of phosphate rock or copper than iron. An electricity requirement of 0.016 kWh per kg crude ore and a heat requirement of 0.058 MJ per kg crude are consequently used. This leads to an energy requirement for beneficiation of 0.088 kWh electricity and 1.12 MJ heat (assumed to be supplied from a fuel-oil furnace) per kg rare earth concentrate with 70% REO.

To condition the bastnasite ore, steam is used for heating the crude ore (slurry with 30-35% solids) before flotation. According to Gupta & Krishnamurthy (2005), in the Molycorp process this treatment is carried out at 70 to 90°C and lasts for about two hours. Other treatments performed at only 40 to 45°C were developed for bastnasite in order to save energy without impairing the separation results (Valdiviezo & Lins, 1997). No information is available on the temperature used for conditioning the ore processed in China. For calculating the steam requirement, it is assumed that the ore slurry containing 30% solids is heated at 25°C, which leads to a steam requirement of 0.09 kg per kg crude ore or 1.8 kg per kg rare earth concentrate with 70% REO.

In order to include all the important emissions from energy use, the energy requirement is linked to the corresponding furnace process, steam production process and electricity mix.

Treatment chemicals for mining and beneficiation

For blasting during mining operations, a value of 0.1 kg of explosives per ton of crude ore is used as for the iron mining described in Classen et al. (2007). An amount of 1.8 g of explosives is calculated per kg of rare earth concentrate.

Various auxiliary materials are used to recover the bastnasite concentrate from the crude ore depending on the ore and the process used. Data from various sources are analysed (Gupta & Krishnamurthy, 2005). The data considered are summarised in Tab. 70.6. Thus 0.058 kg Na₂CO₃, 0.058 kg Na₂CO₃, 0.019 kg fatty acids and 0.62 kg HCl per kg rare earth concentrate are accounted for ore beneficiation (19.44 kg crude ore per kg rare earth concentrate).

Tab. 70.6 Treatment chemicals for mining and beneficiation of rare earth concentrate

Property	Unit	Source 1	Source 2	Source 3	Used in this study	
Conditioner (soda ash: Na ₂ CO ₃)	kg/t ore	3-4	3	2-4	3	Na₂ CO₃
Depressing agent (e.g. Na ₂ SiF ₆ , NaSiO ₃)	kg/t ore	3.5-4.5 *)	3.2 *)	0.5-5 *)	3	NaSiO₃
Collector emulsion (tall oil, fatty acid)	kg/t ore	3-4	0.3	0.2-1	1	fatty acid
Leaching agent (hydrochloric acid 10%)	kg/t ore	n.a.	n.a.	n.a.	3.2 **) HCL	

Source 1: Gupta & Krishnamurthy (2005), Molycorp process
Source 2: Valdiviezo & Lins (1997), Molycorp process
Source 3: Bulatovic (2005), Values from different process schemes shown as range
*) Weight of different agents added (e.g. Na₂SiF₆ and ammonium lignin sulphonate)
**) Calculated amount to reduce pH value caused by alkaline conditioner and depressing agent

Water resources

No detailed information is available on the water consumption of the mining operations. According to Cohen (2005), the water consumption is around 100 litre per tonne of feed if the material is washed. Classen et al. (2007) give a value of 0.002 litre per kg crude ore for iron ore beneficiation, 0.23 litre per kg crude ore for bauxite mining and 1 litre per kg crude ore for copper ore beneficiation. According to Tobin (1998) 0.47 litre water per kg mined material (including overburden) is used for processing the ore in the rare earth mine at Mountain Pass (USA). In EPA (1998c) an average value of 24 kg spent surface impoundment liquids per kg rare earth oxide is given. It is assumed that 20% of the used process water has to be replaced by fresh water. Therefore 20% of the value given in EPA (1998c) is used for the calculations. This assumption leads to a fresh water demand of 4.8 litre per kg rare earth oxide or 3.4 litre per kg rare earth concentrate.

70.6.4 Emissions

Emissions to air

CO₂, CO, SO₂, NO_x and other emissions caused by the burning of fuel are included in the linked energy processes.

No information is available on dust emissions from the mining operations. Classen et al. (2007) give dust emissions of 0.0013 kg per kg crude ore for bauxite mining, 0.001 kg per kg crude ore for iron mining and 0.0005 kg per kg crude ore for copper mining. The value from iron mining of 0.001 kg per kg crude ore or 0.02 kg per kg rare earth concentrate is used as an approximation for this inventory. The following particle size distribution is used analogously to iron mining (Althaus et al. 2004)): 50% for > 10 µm, 45% for 2.5-10 µm and 5% for < 2.5 µm particle size. A similar distribution is given in EPA (1998a) for dust emissions from unpaved roads.

Bastnasite, which makes up about 10% of the processed ore material, has a thorium oxide content ranging from 0.02% to more than 1% (average: ~0.2%). According to EPA (1998b), the activity of bastnasite ranges up to 0.26 kBq/kg (average: 0.067 kBq/kg) for uranium 238, from 0.93 to 86.2 kBq/kg (average: 25 kBq/kg) for thorium 232 and from 0.21 to 120 kBq/kg (average: 5 kBq/kg) for radium 226. Assuming that 10% is also bastnasite within the dust emissions of 20 g per kg rare earth concentrate, the following radioactive emissions to air are calculated per kg of rare earth concentrate: 0.134 Bq uranium 238, 50.6 Bq thorium 232 and 10 Bq radium 226.

Emissions to water

According to Lynas (2006a), water emissions occur in the Chinese Baotou mine due to overflows from the tailings dam. In EPA (1998c) an average value of 24 kg spent surface impoundment liquids per kg rare earth oxide is given. According to Tobin (1998) it is estimated that 20% of this liquid leaks into

the aquifer. In EPA (1998c) an analysis of the spent surface impoundment liquids is given, from which the emissions to ground water are calculated (Values see Tab. 70.7). The emissions of uranium 238, thorium 232 and radium 226 are calculated from the amount of suspended solids assuming identical activities as used for dust emissions. Further emissions to water occur during the processing of the rare earth concentrate which is discussed in section 70.7.4.

Wastes

No information is available on wastes and waste processing for the mining and beneficiation processes. Tailings and magnetic fractions represent possible waste streams from the extraction and concentration of rare earths. It is assumed that the overburden and tailings are backfilled into the mine and are consequently not treated as waste, although finer fractions and possibly increased weathering may lead to greater amounts of components of the backfilled material getting into the ground water compared to the situation before the mining activity.

70.6.5 Land use

No specific information is available on disturbed and rehabilitated land per ton of mined rare earth concentrate. The land use is approximated with data from iron ore mining. Classen et al. (2007) use a value of $7.5 * 10^{-7} \text{ m}^2$ for land transformation and $4.2 * 10^{-5} \text{ m}^2\text{a}$ for land occupation per kg crude ore in the case of iron mining.

A value of $1.45 * 10^{-5} \text{ m}^2$ for land transformation and $8.2 * 10^{-4} \text{ m}^2\text{a}$ for land occupation per kg of rare earth concentrate is calculated from this data (19.44 kg crude ore per kg rare earth concentrate). For the re-cultivation of the mine site, the process of “re-cultivation, iron mine” is used as an approximation ($1.45 * 10^{-5} \text{ m}^2$ per kg rare earth concentrate).

70.6.6 Transport processes

The transport of the auxiliary material to the beneficiation plant is considered with the standard distances for base chemicals (100 km by road and 600 km by rail, respectively 200 km by rail for HCL) because no specific transport distances are available. On the basis of this assumption, 0.22 tkm for road transport and 0.494 tkm for rail transport are included in the inventory.

70.6.7 Infrastructure

No data are available on the mining infrastructure. The infrastructure for the mine is therefore approximated with the “iron mine” process which characterises a mine with an output of $40 * 10^6$ tons of iron ore per year over 30 years. Due to the smaller ore concentration for rare earth mining, a 6.8 times higher infrastructure demand is assumed. This leads to an infrastructure demand of $5.7 * 10^{-12}$ “iron mine” units per kg rare earth concentrate.

70.6.8 Data quality considerations

Tab. 70.7 shows the unit process raw data and data-quality indicators of the inventory of rare earth concentrate from bastnasite, at mine.

A simplified approach with a pedigree matrix is used to calculate the standard deviation. However, the basic uncertainty is adjusted when necessary to represent the ranges of the data obtained from a study of the literature. The inventory is based on only a few sources and approximations with data from similar mining operations are often used. Due to these approximations, the highest uncertainties exist for

particle emissions, fresh water use and land use. The missing emissions to water due to a lack of data also lead to further uncertainty for the emissions. Large uncertainties exist for the infrastructure.

Tab. 70.7 Unit process raw data of rare earth concentrate from bastnasite, at mine

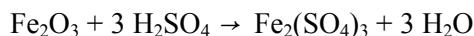
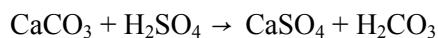
	Name	Location	InfrastructureProcess	Unit	rare earth concentrate, 70% REO, from bastnasite, at beneficiation	UncertaintyType	StandardDeviation95 %	GeneralComment
product	rare earth concentrate, 70% REO, from bastnasite, at beneficiation	CN 0 kg		1				
technosphere	diesel, burned in building machine	GLO 0	MJ	1.00E-1	1	1.69	(4,5,3,3,4,5); estimation based on phosphare mining	
	electricity, medium voltage, at grid	CN 0	kWh	1.45E-1	1	1.69	(4,5,3,3,4,5); estimation based on phosphare mining	
	heavy fuel oil, burned in industrial furnace 1MW, non-modulating	RER 0	MJ	1.12E+0	1	1.69	(4,5,3,3,4,5); estimation based on phosphare mining	
	steam, for chemical processes, at plant blasting	RER 0	kg	1.80E+0	1	1.69	(4,5,3,3,4,5); estimation based on similar process	
	soda, powder, at plant	RER 0	kg	1.80E-3	1	1.38	(4,5,2,3,3,3); data from iron mining used as proxy	
	sodium sulphate, powder, production mix, at plant	RER 0	kg	5.80E-2	1	1.63	(2,3,5,3,3,5); data for similar process	
	fatty acids, from vegetarian oil, at plant	RER 0	kg	5.80E-2	1	1.63	(2,3,5,3,3,5); data for similar process	
	hydrochloric acid, 30% in H ₂ O, at plant	RER 0	kg	6.20E-1	1	2.15	(4,5,nA,nA,nA,5,5); calculated value	
	transport, lorry >16t, fleet average	RER 0	tkm	2.20E-1	1	2.09	(4,5,nA,nA,nA,nA); standard distances used	
	transport, freight, rail	RER 0	tkm	4.94E-1	1	2.09	(4,5,nA,nA,nA,nA); standard distances used	
	mine, iron	GLO 1	unit	5.70E-12	1	3.18	(4,5,2,2,3,5); data from iron mining used as proxy	
	recultivation, iron mine	GLO 0	m2	1.45E-5	1	1.45	(4,5,2,2,3,5); data from iron mining used as proxy	
resource, in ground	Cerium, 24% in bastnasite, 2.4% in crude ore, in ground	-	-	kg	4.67E-1	1	1.13	(2,2,2,1,1,4); calculated from ore composition
	Lanthanum, 7.2% in bastnasite, 0.72% in crude ore, in ground	-	-	kg	1.40E-1	1	1.13	(2,2,2,1,1,4); calculated from ore composition
	Neodymium, 4% in bastnasite, 0.4% in crude ore, in ground	-	-	kg	7.70E-2	1	1.13	(2,2,2,1,1,4); calculated from ore composition
	Praseodymium, 0.42% in bastnasite, 0.042% in crude ore, in ground	-	-	kg	8.17E-3	1	1.13	(2,2,2,1,1,4); calculated from ore composition
	Europium, 0.06% in bastnasite, 0.006% in crude ore, in ground	-	-	kg	1.17E-3	1	1.13	(2,2,2,1,1,4); calculated from ore composition
	Samarium, 0.3% in bastnasite, 0.03% in crude ore, in ground	-	-	kg	5.83E-3	1	1.13	(2,2,2,1,1,4); calculated from ore composition
	Gadolinium, 0.15% in bastnasite, 0.015% in crude ore, in ground	-	-	kg	2.92E-3	1	1.13	(2,2,2,1,1,4); calculated from ore composition
resource, in water	Water, unspecified natural origin	-	-	m3	3.40E-3	1	1.64	(4,5,2,3,4,4); estimation based on similar mining operations
resource, land	Transformation, from unknown	-	-	m2	1.45E-5	1	2.19	(4,5,2,2,3,5); data from iron mining used as proxy
	Transformation, to mineral extraction site	-	-	m2	1.45E-5	1	2.19	(4,5,2,2,3,5); data from iron mining used as proxy
	Occupation, mineral extraction site	-	-	m2a	3.41E-3	1	1.73	(4,5,2,2,3,5); data from iron mining used as proxy
emission air, low population density	Particulates, > 10 um	-	-	kg	1.00E-2	1	1.68	(4,5,2,3,3,3); data from iron- and bauxite mining used as proxy
	Particulates, > 2.5 um, and < 10um	-	-	kg	9.00E-3	1	2.15	(4,5,2,3,3,3); data from iron- and bauxite mining used as proxy
	Particulates, < 2.5 um	-	-	kg	1.00E-3	1	3.14	(4,5,2,3,3,3); data from iron- and bauxite mining used as proxy
	Uranium-238	-	-	kBq	1.34E-4	1	3.41	(4,5,5,3,3,5); estimated from dust emissions
	Thorium-232	-	-	kBq	5.06E-2	1	3.41	(4,5,5,3,3,5); estimated from dust emissions
	Thorium-232	-	-	kBq	1.00E-2	1	3.41	(4,5,5,3,3,5); estimated from dust emissions
	Heat, waste	-	-	MJ	5.74E+0	1	1.69	(4,5,3,3,4,5); calculated from energy demand
emission water, ground-	Aluminum	-	-	kg	1.40E-4	1	5.43	(4,5,3,3,4,5); data only from one source and based on estimates
	Iron, ion	-	-	kg	2.73E-8	1	5.43	(4,5,3,3,4,5); data only from one source and based on estimates
	Chromium, ion	-	-	kg	5.25E-5	1	3.38	(4,5,3,3,4,5); data only from one source and based on estimates
	Lead	-	-	kg	5.26E-5	1	5.43	(4,5,3,3,4,5); data only from one source and based on estimates
	Manganese	-	-	kg	1.40E-5	1	5.43	(4,5,3,3,4,5); data only from one source and based on estimates
	Suspended solids, unspecified	-	-	kg	7.70E-4	1	1.94	(4,5,3,3,4,5); data only from one source and based on estimates
	TOC, Total Organic Carbon	-	-	kg	2.31E-7	1	1.94	(4,5,3,3,4,5); data only from one source and based on estimates
	Uranium-238	-	-	kBq	5.16E-6	1	3.59	(4,5,5,3,4,5); estimation, high uncertainty
	Thorium-232	-	-	kBq	1.95E-3	1	3.59	(4,5,5,3,4,5); estimation, high uncertainty
	Radium-226	-	-	kBq	3.85E-4	1	3.59	(4,5,5,3,4,5); estimation, high uncertainty

70.7 Production of rare earth oxides from bastnasite

70.7.1 Process

This process includes roasting and cracking of the rare earth concentrate and the following separation of the various rare earth oxides.

In China, the bastnasite concentrates are processed by heating with 98% sulphuric acid to 500°C in a rotary kiln. This roasting process removes the fluorocarbonate content of the ore. Besides hydrofluoric acid gases and carbon dioxide, sulphur dioxide is also emitted.



The rare earths are precipitated as a double sodium sulphate by leaching with water and adding sodium chloride. In a further process step, the rare earth sulphates are converted with caustic soda to hydroxides and are then dissolved in hydrochloric or nitric acid (Gupta & Krishnamurthy, 2005).

Mixtures derived from the mineral cracking are further processed to separate the individual elements. Because of the generally similar chemical properties of the rare earths, their separation can be time-consuming and expensive. Multi-stage solvent extraction (SX) is used for the separation and results in materials of up to 99.9% purity (Sinton, 2006). According to Doyle et al. (2000), 30 to 60 separation stages are needed to obtain pure products. On the basis of a process scheme presented in Wenli et al. (2000) for a Chinese bastnasite, it is assumed that around 90 to 180 stages are needed for the processes covered in this inventory.

The extractants used for solvent extraction are typically esters of phosphoric acid, such as di-2-ethylhexyl phosphoric acid (DEHPA). Depending on the specific rare earth element to be separated and the process used, various other extractants may also be used. After separation by solvent extraction into individual solutions containing rare earths, a precursor is precipitated out: this is usually oxalate. The desired oxide is produced after calcination at 1000 °C.

A simplified process flowchart for rare earth oxide production from bastnasite is shown in Fig. 70.5.

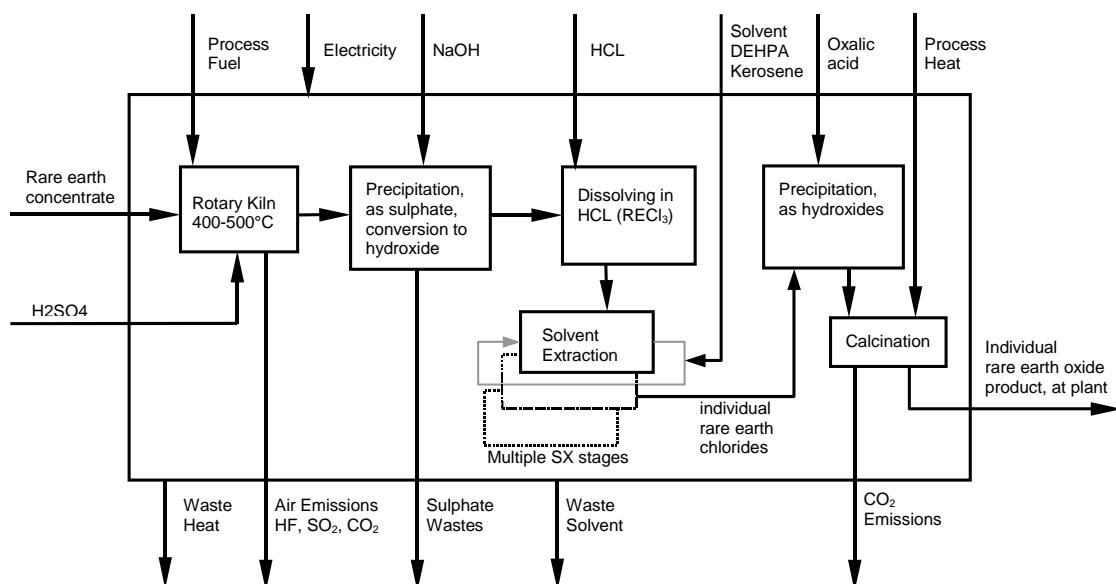


Fig. 70.5 Simplified process flowchart for rare earth oxide production from bastnasite

70.7.2 Resources

The input to this process is the bastnasite rare earth concentrate with a rare earth oxide (REO) content of 70%. For the roasting and separation process, a typical recovery rate of 84 to 96 percent of the rare earth oxides is given (Lynas 2006a, Patersons 2006, Gupta & Krishnamurthy 2005). A yield of 90 percent is used. To obtain 1 kg of rare earth oxide product therefore, 1.59 kg of rare earth concentrate are needed.

70.7.3 Energy use and auxiliaries

Process energy use for beneficiation

In order to remove fluorocarbonate from the bastnasite concentrate, it is roasted at about 500°C before further processing with solvent extraction. The energy requirement for this roasting process as well as the final calcination is approximated with data from phosphate rock beneficiation due to lack of specific process data. A heat requirement of 0.34 MJ per kg feed for each process step is calculated from the values presented in Landbank (1994). For the roasting process, 0.98 MJ per kg of rare earth oxide product (2.89 kg feed) are accounted, and 0.49 MJ per kg rare earth oxide product (1.44 kg feed) for the final calcination.

No information is available on the electricity consumption of the separation process. Due to the large amount of liquids pumped, its value will not be negligible. According to Kessler (1985), the electricity requirement of a similar solvent extraction process for vegetable oils uses 55 kWh per ton of feed material. For the rare earth separation process investigated here, at least four separation steps are needed to obtain the desired products. An electricity requirement of 0.22 kWh per kg of input material or 0.35 kWh per kg of rare earth oxide is consequently used.

Auxiliaries used

The auxiliary materials requirement is calculated from the stoichiometric amount assuming a process efficiency of 95%. For the cracking process, 1.3 kg of concentrated sulphuric acid, 0.7 kg of caustic soda (active substance) and 0.45 kg of hydrochloric acid are used per kg of rare earth oxide product. Another 0.55 kg of oxalic acid is accounted for the precipitation of the extracted rare earth products.

The aqueous solutions used for solvent extraction have concentrations of about 100–140 g REO per litre. About 60 to 80 litres of organic extractant are used per kg of rare earth oxide content (Yoshida & Nakayama, 2001). No information is available on the recovery rate of the organic extractant. Due to the multi-stage solvent extraction process, large amounts of extractant will also be used with a very good recovery rate. If a solvent waste rate of 0.05% per extraction stage and a process with 120 extraction stages is assumed, around 4.8 kg of waste solvent are generated per kg of extracted rare earth product.

According to EPA (1998c), it is estimated that between 0.006 and 6.1 kg of waste solvent per kg REO are generated within the scope of rare earth cracking and separation. An average value of 3 kg per kg REO is given in EPA (1998c). This solvent has to be replaced by a similar amount of fresh solvent.

A usual composition of the extractant is 70 vol-% kerosene and 30 vol-% di(2-ethylhexyl)phosphoric acid (DEHPA) or similar organo-phosphoric acids. An average solvent extractant requirement of 3 kg per kg REO consisting of 2 kg kerosene and 1 kg DEHPA (approximated with “organic chemical”) is used.

Tab. 70.8 Energy and auxiliaries use in rare earth oxide production from bastnasite

	Unit	Used in this Inventory	Stoichiometric calculation	Remarks / Source
Heat, heavy fuel oil	MJ	1.47	-	Phosphate rock production (Landbank 1994)
Electricity	kWh	0.35	-	Estimation from vegetable oil SX (Kessler 1985)
Sulphuric acid	kg	1.3	1.05	Ore cracking; 5% excess included
Caustic soda	kg	0.7	0.66	Conversion to hydroxides, 5% excess included
Hydrochloric acid	kg	0.45	0.52	Dissolving hydroxides, 5% excess included
Organic chemicals	kg	0.55	0.0541	Precipitation (oxalic acid), 5% excess included
Kerosene	kg	2 *)	-	SX process, estimation based on (EPA, 1998c)
Organic chemicals	kg	1 *)	-	SX process, estimation based on (EPA, 1998c)

*) Range of values for total solvent use 0.006 to 6.1 kg/kg REO according to estimation in EPA (1998c)

70.7.4 Emissions

Emissions to air

Emissions to air are included in the linked unit processes for energy use, but additional process emissions also occur. The fluorine in the bastnasite is emitted during roasting. According to Sinton (2006), Chinese rare earth concentrate contains 6.4 to 9.8 percent of fluorine. For the composition used, 0.108 kg of fluorine emissions (as HF) per kg of rare earth oxide product is calculated. It is assumed that the roasting process includes emission control. According to EPA (1993), a scrubber has a removal efficiency of 80 to 99 percent. Venturi fume scrubbers typically achieve a 95% removal efficiency in a single stage. This removal efficiency is used in this inventory, which leads to a figure of 5.4 g fluorine emissions (as HF) per kg of rare earth concentrate.

It is further reported that emissions of sulphur dioxide occur. No emission value is available for these. For this inventory it is assumed that the excess sulphur from the sulphuric acid used in the roasting process is emitted as SO₂. This assumption leads to a figure of 18 g of SO₂ emissions (uncontrolled). When a scrubber with 95% removal efficiency is also applied to these emissions, this leads to 0.9 g of SO₂ emissions per kg of rare earth oxide product.

The decomposition of the carbonate in the bastnasite concentrate and the organic precipitant produces carbon dioxide emissions within the roasting and calcination processes. Emissions of 0.855 kg CO₂ per kg of rare earth oxide product are calculated for this process.

Emissions to water

Only scant information is available on emissions to water and waste materials. According to EPA (1998c), around 0.85 kg of processing solution and 0.425 kg of process waste water are produced per kg of rare earth oxide (REO). Information on the composition of this waste water (as concentration in ppm) is also given in EPA (1998c). The emissions of uranium 238, thorium 232 and radium 226 are calculated from the amount of suspended solids assuming an identical activities as used for dust emissions during rare earth mining (see section 70.6.4). As environmental problems caused by emissions to water from rare earth processing are mentioned (Lynas 2006a), it is assumed that this waste water is discharged into a river. The emissions calculated from the concentration and the amount of waste water are reported in Tab. 70.10.

Wastes

According to EPA (1998c), large amounts of waste solvent may be produced. The figures given are estimates and cover a range from a low value of 0.006 kg per kg REO to 6.1 kg per kg REO (average of 3 kg per kg REO). Our own calculation based on a process scheme given in Yoshida & Nakayama (2001) and assuming a process with 120 stages and a 99.5% solvent recovery rate in each stage yields a figure of 4.8 kg of waste solvent per kg REO. A value of 3 kg per kg REO is used. It is assumed that the waste solvent is incinerated in a hazardous waste incineration plant.

Sulphate wastes are generated in the cracking and precipitation steps. A total amount of 1.97 kg (dry weight) per kg of rare earth oxide product is calculated. It is assumed that this waste is landfilled. The waste is approximated with the process “disposal, sulphidic tailings, off-site”.

70.7.5 Transport processes

The transport of rare earth concentrate and auxiliary material to the separation plant is considered using the standard distances for base chemicals (100 km by road and 600 km by rail) because no specific transport distances are available. On the basis of this assumption, 0.759 tkm of road transport and 4.37 tkm of rail transport are included.

The transport the auxiliary materials to the separation is considered using the standard distances for base chemicals (100 km by road and 600 km by rail, respectively 200 km by rail for HCL) because no specific transport distances are available. The transport of the rare earth concentrate from the mine in Bayan Obo to the separation plant in Baotou is carried out on railway between the two locations. A distance of 130 km by rail is included for the transport of the rare earth concentrate. On the basis of these assumptions, 0.775 tkm of road transport and 4.26 tkm of rail transport are included.

70.7.6 Infrastructure

No data are available for the infrastructure of the rare earth separation plants. According to HeFa (2006), one of the largest rare earth processing plants in China has a production capacity of 15,000 t/year rare earth products and covers an area of 270,000 m². This leads to a specific land use of 18 m²/(t/a). This high figure is probably due to the complex multi-stage separation processes. The infrastructure for the process is approximated with the process “chemical plant, organics” (specific land use 1.05 m²/(t/a)). In order to cover the complex process infrastructure for rare earth separation, an infrastructure requirement of $69 * 10^{-10}$ units “chemical plant, organics” per kg rare earth oxide product is used.

70.7.7 Allocation of rare earth oxide products

The fact that rare earths are co-produced creates a situation where one or two elements that are in particular demand require other elements to be mined as well. Neodymium is one element that appears to create this situation due to its use in neo magnets.

Various rare earth oxides are separated from the rare earth concentrate. In the production process described here, 1 kg of processed rare earth oxide consists on average of 0.493 kg cerium oxide, 0.282 kg lanthanum oxide, 0.154 kg neodymium oxide, 0.051 kg praseodymium oxide and 0.02 kg samarium-europium-gadolinium concentrate. The energy input, emissions and infrastructure expenditures are allocated to these products.

Various concepts may be employed for the allocation. The revenue is employed as an allocation scheme. In such a case, a product with a higher specific value is assigned a higher environmental burden than a product with a low price. The allocation factors are determined according to the average bulk prices for cerium oxide, lanthanum oxide, neodymium oxide and praseodymium oxide between 2004 and 2006 (Lynas, 2006b). The price for the samarium-europium-gadolinium concentrate is based on

data from CREIW (2002) from February 2002. Tab. 70.9 summarises the resulting allocation factors and underlying assumptions.

In order to maintain the mass balance for the input material, the rare earth concentrate input is allocated according to the mass of the product output.

Tab. 70.9 Allocation factors applied to rare earth oxide production from bastnasite

	Amount [kg]	Value [\$/kg] *)	Allocation factor
Cerium concentrate, 60% cerium oxide, at plant	0.493	1.5	22.1 %
Lanthanum oxide, at plant	0.282	1.75	14.7 %
Neodymium oxide, at plant	0.154	8.9	40.9 %
Praseodymium oxide, at plant	0.051	9.6	14.6 %
Samarium europium gadolinium concentrate, 94% rare earth oxide, at plant	0.020	13 **)	7.8 %

*) Average rare earth oxide bulk prices FOB China, 9.2004 - 9.2006, 99% purity (Lynas, 2006b)
 **) Price for SEG concentrate calculated with data of CREIW (2002) based on Chinese Rare Earth Prices

70.7.8 Data quality considerations

Tab. 70.10 shows the multi-output process raw data and data-quality indicators of the inventory of rare earth oxide production from bastnasite.

A simplified approach with a pedigree matrix is used to calculate the standard deviation. However, the basic uncertainty is adjusted to represent the ranges of the data obtained from a study of the literature or similar processes. Because this data are often approximated with information from similar processes or is calculated from the stoichiometric demand, the uncertainty in the inventory is generally relatively high. The highest uncertainties exist for emissions and wastes, especially the amount of waste solvent generated. Emissions to water also involve a high uncertainty due to a lack of process-specific data. Further uncertainty is due to possibly missing auxiliary materials and further emissions or wastes. Large uncertainties also exist for the data for transport distances and the infrastructure.

Tab. 70.10 Multi-output process raw data of rare earth oxide production from bastnasite

	Name	Location	InfrastructureProcess	Unit	rare earth oxide production from bastnasite	UncertaintyType	StandardDeviation95%	GeneralComment	lanthanum oxide, at plant	cerium concentrate, 60% cerium oxide, at plant	neodymium oxide, at plant	praseodymium oxide, at plant	samarium europium gadolinium concentrate, 94% rare earth oxide, at plant
									CN	CN	CN	CN	CN
									0 kg	0 kg	0 kg	0 kg	0 kg
allocated	lanthanum oxide, at plant	CN	0	kg	2.82E-1				100	0	0	0	0
allocated	cerium concentrate, 60% cerium oxide, at plant	CN	0	kg	4.93E-1				0	100	0	0	0
allocated	neodymium oxide, at plant	CN	0	kg	1.54E-1				0	0	100	0	0
allocated	praseodymium oxide, at plant	CN	0	kg	5.10E-2				0	0	0	100	0
allocated	samarium europium gadolinium concentrate, 94% rare earth oxide, at plant	CN	0	kg	2.00E-2				0	0	0	0	100
technosphere	rare earth concentrate, 70% REO, from bastnasite, at beneficiation	CN	0	kg	1.59E+0	1	1.09	(2,2,1,1,1,3); input 90% yield assumed	28.2	49.3	15.4	5.1	2.0
	electricity, medium voltage, at grid	CN	0	kWh	3.50E-1	1	2.37	(4,5,5,3,5,5); estimation data from oil extraction	14.7	22.0	40.9	14.6	7.8
	heavy fuel oil, burned in industrial furnace 1MW, non-modulating	RER	0	MJ	1.47E+0	1	1.69	(4,5,3,3,4,5); estimation based on phosphoric acid production	14.7	22.0	40.9	14.6	7.8
	sulphuric acid, liquid, at plant	RER	0	kg	1.30E+0	1	1.44	(4,5,nA,nA,3,5); stoichiometric calculated value	14.7	22.0	40.9	14.6	7.8
	sodium hydroxide, 50% in H ₂ O, production	RER	0	kg	7.00E-1	1	1.44	(4,5,nA,nA,3,5); stoichiometric calculated value	14.7	22.0	40.9	14.6	7.8
	hydrochloric acid, 30% in H ₂ O, at plant	RER	0	kg	4.50E-1	1	1.44	(4,5,nA,nA,3,5); stoichiometric calculated value	14.7	22.0	40.9	14.6	7.8
	chemicals organic, at plant	GLO	0	kg	1.55E+0	1	1.48	(4,5,3,5,3,5); estimation on solvent use	14.7	22.0	40.9	14.6	7.8
	kerosene, at refinery	RER	0	kg	2.00E+0	1	1.48	(4,5,3,5,3,5); estimation on solvent use	14.7	22.0	40.9	14.6	7.8
	transport, lorry >16t, fleet average	RER	0	tkm	7.75E-1	1	2.09	(4,5,nA,nA,nA,nA); standard distances used	14.7	22.0	40.9	14.6	7.8
	transport, freight, rail	RER	0	tkm	4.26E+0	1	2.09	(4,5,nA,nA,nA,nA); standard distances used	14.7	22.0	40.9	14.6	7.8
	disposal, solvents mixture, 16.5% water, to hazardous waste incineration	CH	0	kg	3.00E+0	1	1.48	(4,5,3,5,3,5); estimated input and process route	14.7	22.0	40.9	14.6	7.8
	disposal, sulfidic tailings, off-site	GLO	0	kg	1.97E+0	1	1.48	(4,5,3,5,3,5); estimated process for solid wastes	14.7	22.0	40.9	14.6	7.8
	chemical plant, organics	RER	1	unit	6.90E-9	1	3.18	(4,5,2,2,3,5); chemical plant used as proxy	14.7	22.0	40.9	14.6	7.8
emission air, low population density	Carbon dioxide, fossil	-	-	kg	8.55E-1	1	1.44	(4,5,nA,nA,3,5); calculated from input	14.7	22.0	40.9	14.6	7.8
	Hydrogen fluoride	-	-	kg	5.40E-3	1	1.73	(4,5,nA,nA,3,5); calculated from input, assumed emission control	14.7	22.0	40.9	14.6	7.8
	Sulfur dioxide	-	-	kg	9.00E-4	1	1.44	(4,5,nA,nA,3,5); calculated from input, assumed emission control	14.7	22.0	40.9	14.6	7.8
	Heat, waste	-	-	MJ	1.26E+0	1	1.69	(4,5,3,3,4,5); calculated from inputs	14.7	22.0	40.9	14.6	7.8

Tab. 3.10 Multi-output process raw data of rare earth oxide production from bastnasite (2. Part)

	Name	Location	InfrastructureProcess	Unit	rare earth oxide production from bastnasite	UncertaintyType StandardDeviation95%	GeneralComment	lanthanum oxide, at plant	cerium concentrate, 60% cerium oxide, at plant	neodymium oxide, at plant	praseodymium oxide, at plant	samarium europium gadolinium concentrate, 94% rare earth oxide, at plant
								CN 0 kg	CN 0 kg	CN 0 kg	CN 0 kg	CN 0 kg
								Location InfrastructureProcess Unit				
emission water, river	Aluminum	-	-	kg	3.05E-5	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Antimony	-	-	kg	4.72E-6	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Arsenic, ion	-	-	kg	4.29E-7	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Barium	-	-	kg	4.55E-7	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Beryllium	-	-	kg	4.68E-8	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Cadmium, ion	-	-	kg	4.59E-8	1	3.34 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Chromium, ion	-	-	kg	2.47E-7	1	3.34 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Cobalt	-	-	kg	2.52E-6	1	3.34 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Copper, ion	-	-	kg	9.35E-7	1	3.34 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Iron, ion	-	-	kg	8.68E-6	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Lead	-	-	kg	2.13E-6	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Magnesium	-	-	kg	1.82E-3	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Manganese	-	-	kg	8.84E-5	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Mercury	-	-	kg	2.13E-10	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Molybdenum	-	-	kg	4.25E-7	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Nickel, ion	-	-	kg	1.06E-6	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Selenium	-	-	kg	4.29E-7	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Silver, ion	-	-	kg	4.42E-7	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Thallium	-	-	kg	2.13E-6	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Vanadium, ion	-	-	kg	4.25E-7	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Zinc, ion	-	-	kg	6.89E-6	1	5.39 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Cyanide	-	-	kg	3.83E-8	1	3.34 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Sulfide	-	-	kg	1.45E-7	1	1.90 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Sulfate	-	-	kg	9.21E-4	1	1.90 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Fluoride	-	-	kg	1.28E-5	1	1.90 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Chloride	-	-	kg	6.14E-3	1	3.34 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Suspended solids, unspecified	-	-	kg	4.03E-3	1	1.90 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	TOC, Total Organic Carbon	-	-	kg	4.64E-5	1	1.90 (3,5,3,3,4,5); data only from one source	14.7	22.0	40.9	14.6	7.8
	Uranium-238	-	-	kBq	2.70E-4	1	3.59 (4,5,5,3,4,5); estimation, high uncertainty	14.7	22.0	40.9	14.6	7.8
	Thorium-232	-	-	kBq	1.02E-1	1	3.59 (4,5,5,3,4,5); estimation, high uncertainty	14.7	22.0	40.9	14.6	7.8
	Radium-226	-	-	kBq	2.01E-2	1	3.59 (4,5,5,3,4,5); estimation, high uncertainty	14.7	22.0	40.9	14.6	7.8

70.8 Cumulative results and interpretation

70.8.1 Introduction

Selected LCI results and values for the cumulative energy requirement are presented and discussed in this section. Please note that only a small part of the 1500 elementary flows is presented here. The selection of the elementary flows shown in the tables is not based on their environmental relevance. Rather, it allows the contributions of the different life cycle phases or specific inputs from the technosphere to the selected elementary flows to be illustrated. Please refer to the *ecoinvent* database for the complete LCIs.

The selection shown is unsuitable for a life-cycle assessment of the analysed processes and products. Please download data from the database for your own calculations, not least because of possible minor deviations between the presented results and the database due to corrections and changes made in the background data used as inputs to the relevant dataset.

The *ecoinvent* database also contains the results of life-cycle impact assessments. Assumptions and interpretations are necessary to match current LCIA methods to the *ecoinvent* inventory results. They are described in Frischknecht et al. (2007). You are strongly advised to read the respective sections of the implementation report before applying the LCIA results.

70.8.2 Selected LCI results

Process “rare earth concentrate from bastnasite, at mine”

The major part of the carbon dioxide (50%), NMVOC (32%), nitrogen oxide emissions (34%) and the cumulative energy demand (fossil: 53%) are caused by energy and fuel used for the mining and processing of the mineral. The hydrochloric acid used to remove calcite also has an important impact on these emissions (25-40%) and the cumulative energy demand (fossil: 38%, nuclear: 87%). The dust emissions of the production cause 98% of the total particle emissions and 68% of the emissions of particulate < 2.5µm. For the land use, The fatty acids used for flotation are with 69% the most important impact for the land use. The land use of the mining process itself is with 3% of minor importance.

Tab. 70.11 shows selected LCI results and cumulative energy demands for the mining process “rare earth concentrate from bastnasite, at mine”.

Multi-output process “rare earth concentrate from bastnasite, at mine”

The major part of the carbon dioxide (54%), NMVOC (76%), nitrogen oxide emissions (41%), the cumulative energy demand (fossil: 74%, nuclear: 30%) and the land use (54%) are caused by solvent used for the multi-stage solvent extraction (production and disposal). The rare earth concentrate as raw material also has an important impact on these emissions (11-22%) and the cumulative energy demand (fossil: 11%, nuclear: 21%). The major part of the dust emissions also origin from the mining of the raw material (48%).

Tab. 70.11 shows selected LCI results and cumulative energy demands for the multi-output process “rare earth oxide production from bastnasite”. The results for the different rare earth oxides presented in Tab. 70.11 depend significantly on the chosen allocation method.

Tab. 70.11 Selected LCI results and the cumulative energy demand for rare earth oxide production from bastnasite

Ecocat	Ecosubcat	Name	Name	rare earth concentrate, 70% REO, from bastnasite, at beneficiation	cerium concentrate, 60% cerium oxide, at plant	lanthanum oxide, at plant	neodymium oxide, at plant	praseodymium oxide, at plant	samarium europium gadolinium concentrate, 94% rare earth oxide, at plant
			Location Unit	CN kg	CN kg	CN kg	CN kg	CN kg	CN kg
cumulative energy demand	fossil	non-renewable energy resources, fossil	MJ-Eq	1.93E+01	1.43E+02	1.62E+02	6.99E+02	7.51E+02	1.01E+03
	nuclear	non-renewable energy resources, nuclear	MJ-Eq	3.84E+00	1.60E+01	1.77E+01	6.52E+01	6.98E+01	9.29E+01
	primary forest	non-renewable energy resources, primary forest	MJ-Eq	8.99E-02	1.43E-01	1.43E-01	1.43E-01	1.44E-01	1.44E-01
	water	renewable energy resources, water	MJ-Eq	5.72E-01	2.32E+00	2.56E+00	9.31E+00	9.96E+00	1.32E+01
	biomass	renewable energy resources, biomass	MJ-Eq	1.30E+00	2.90E+00	3.04E+00	7.00E+00	7.39E+00	9.31E+00
	wind	renewable energy resources, kinetic (in wind), converted	MJ-Eq	6.85E-02	2.65E-01	2.91E-01	1.03E+00	1.11E+00	1.47E+00
	geothermal	renewable energy resources, geothermal, converted	MJ-Eq	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	solar	renewable energy resources, solar, converted	MJ-Eq	9.80E-04	3.79E-03	4.17E-03	1.48E-02	1.59E-02	2.11E-02
selected LCI results	resource	land occupation	m2a	1.38E-01	4.07E-01	4.38E-01	1.33E+00	1.42E+00	1.86E+00
	air	CO2, fossil	kg	1.31E+00	7.14E+00	7.99E+00	3.22E+01	3.45E+01	4.63E+01
	air	NMVOC	kg	7.51E-04	5.63E-03	6.38E-03	2.76E-02	2.97E-02	4.00E-02
	air	nitrogen oxides	kg	3.43E-03	1.41E-02	1.55E-02	5.69E-02	6.09E-02	8.10E-02
	air	sulphur dioxide	kg	4.74E-03	2.78E-02	3.12E-02	1.28E-01	1.37E-01	1.85E-01
	air	particulates, <2.5 um	kg	1.47E-03	3.46E-03	3.65E-03	9.01E-03	9.53E-03	1.21E-02
	water	BOD	kg	1.72E-03	3.20E-02	3.70E-02	1.77E-01	1.91E-01	2.59E-01
	soil	cadmium	kg	4.95E-09	1.08E-08	1.13E-08	2.53E-08	2.66E-08	3.34E-08

70.9 Conclusions

The solvent demand for the multi-stage solvent extraction used for rare earth oxide production has a large influence on the total environmental impact. Due to a lack of accurate process-specific data on the solvent use this will be the main uncertainty of the results.

Depending on the specific mineral source and the production site the production process may be different. Such differences were not considered. The process described covers only the process used in China to crack and separate Baotou bastnasite.

70.10 Appendices: EcoSpold Meta Information

Tab. 70.12 EcoSpold Meta Information for rare earth oxide production from bastnasite

ReferenceFunction	Name	rare earth concentrate, 70% REO, from bastnasite, at beneficiation	rare earth oxide production from bastnasite
Geography	Location	CN	CN
ReferenceFunction	InfrastructureProcess	0	0
ReferenceFunction	Unit	kg	kg
DataEntryBy	DataSetInformer	Type	1 5
		Version	2.0 2.0
		energyValues	0 0
		LanguageCode	en en
		LocalLanguageCode	de de
	Person	72	72
	QualityNetwork	1	1
ReferenceFunction	DataSetRelatesToProduct	1	1
	IncludedProcesses	The process includes material and energy input, emissions and land use for the mining and concentration of a bastnasite ore with a rare earth oxide concentration of 6%. Transport and infrastructure are estimated.	The process includes raw materials, processing chemicals and processing energy, emissions to water and wastes. Transport and infrastructure are estimated. The multi output-process "rare earth oxide production from bastnasite" delivers the co-products "cerium concentrate, 60% cerium oxide, at plant", "lanthanum oxide, at plant", "neodymium oxide, at plant", "praseodymium oxide, at plant", "samarium europium gadolinium concentrate 94% rare earth oxide, at plant". The revenue is used as allocation scheme.
	Amount	1	1
	LocalName	Seltene Erden Konzentrat, 70% REO, aus Basträsit, ab Aufbereitung	Seltene Erden Oxid-Produktion aus Bastnäsit
	Synonyms		
	GeneralComment	In- and outputs are calculated from bastnasite ore composition mined in China. Infrastructure and land use approximated with iron ore mining. Some inputs of auxiliary materials are calculated according to stoichiometry. Rough estimation for energy consumption, wastes and emissions.	In- and outputs are calculated for rare earth oxide processing with sulphuric acid as used in China. Infrastructure approximated with a chemical plant. Some inputs of auxiliary materials are calculated according to stoichiometry. Rough estimation for energy consumption, solvent use and waste generation.
	InfrastructureIncluded	1	1
	Category	chemicals	chemicals
	SubCategory	inorganics	inorganics
	LocalCategory	Chemikalien	Chemikalien
	LocalSubCategory	Anorganika	Anorganika
	Formula		
	StatisticalClassification		
	CASNumber		
TimePeriod	StartDate	2000	2000
	EndDate	2005	2005
	DataValidForEntirePeriod	1	1
	OtherPeriodText		
Geography	Text	Production in China considered. Process applicable for other regions if a similar ore type is used.	Production in China considered. Process applicable for other regions if a similar process is used.
Technology	Text	Mineral concentration by froth flotation to rare earth concentrate product with 70% rare earth oxide (REO). Leaching of concentrate with HCl included but no calcination. Composition of product: SiO ₂ 1.0%, CaO 1.0%, BaO 1.0%, F 8.0%, SiO ₂ 0.4%, Fe ₂ O ₃ 0.5%, P ₂ O ₅ 1.0%, MgO 0.4%, ThO ₂ 0.1%, CO ₂ 20.0%, -O = F ₂ : -	Process includes roasting and cracking of the rare earth concentrate with 98% sulphuric acid at 500°C in a rotary kiln. For the following separation of the different rare earth oxides solvent extraction (SX) is used. The obtained rare earth oxide product has a purity of up to 99.9%.
Representativeness	Percent	45	45
	ProductionVolume	unknown	unknown
	SamplingProcedure	based on literature	based on literature
	Extrapolations	none	none
	UncertaintyAdjustments	none	none
DataGeneratorAuthor	Person	72	72
	DataPublishedIn	2	2
	ReferenceToPublishedSource	8	8
	Copyright	1	1
	AccessRestrictedTo	0	0
	CompanyCode		
	CountryCode		
	PageNumbers	Rare earth	Rare earth
	Validator	42	42
	Details	automatic validation in Excel	automatic validation in Excel
ProofReading	OtherDetails	none	none

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71 Silicones and Silicone Products

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Last change v1.3, 2006

Acknowledgement

We thank Dr. Walter Held, Wacker-Silicones, DE for the information provided in a personal communication.

Summary

Silicones are a diverse family of materials that combine the temperature and chemical resistance of glass with the versatility of plastics. The manufacturers produce a range of thousands of different products in interlinked processes. The unit process raw data are investigated for an average silicone product in plants manufacturing the raw materials of interest. The inventory for average silicone products is meant to be used as a background information in inventories where these products make only a small part of the inputs. This inventory can give an approximation of the environmental impacts due to the production of these raw materials. For a detailed analysis and the direct comparison of a specific silicone product with another material further investigation would be necessary.

71.1 Introduction

Silicones¹ are a diverse family of materials that combine the temperature and chemical resistance of glass with the versatility of plastics. They are used to enhance the performance of thousands of products in virtually every major industry.

There are two products of interest for which unit process data shall be investigated. Silicone rubber is the basic product for the production of tubes. Silicone sealants are a common product used in the building industry e.g. for fixing window glasses to the frame. Both products are used for the manufacturing of solar collectors. Unfortunately not enough data were available for the specific production routes. Thus the final inventory is investigated for an average silicone product.

The basic products MG-silicon (metal grade), silicon carbide, silicon tetrachloride and the production of electronic-grade (EG), solar-grade (SoG) silicon and silicon wafers for photovoltaic appliances is investigated for this project in (Jungbluth 2003).

71.2 Reserves and Resources of Material

Silica sand is the basic material for the production of silicone products. A lot of process stages are necessary for purifying the material and for producing the final products.

71.3 Characterisation of Material

Several thousand silicon products are produced. The following basic intermediate products can be distinguished. An overview about the different production routes is shown in Fig. 71.2:

- Hyperpure polycrystalline silicon: elemental silicon used in computer chips and other electronic devices. This basic product is not investigated in this section.

¹ The spelling “silicone” is used for the organic compounds while “silicon” is used for the metal and inorganic compounds of silicon.

- Silanes: Silanes are an important class of silicone compounds. They are produced by reaction of silicon and methyl chloride. These critical intermediates serve both as internal building blocks but also as useful products for the chemical and electronic industries (Fig. 71.1).
- Silicones, known chemically as polyorganosiloxanes or siloxanes, have a structure similar to that of organically modified quartz, with a backbone consisting of alternating silicon and oxygen atoms (Fig. 71.1). They are produced from silanes. Silicones have a unique chemical structure that allows them to be produced in a wide variety of forms. The properties of silicones are determined by the parent silane. Monofunctional silanes yield low-molecular silicones and difunctional silanes yield high-molecular ones. When trifunctional silanes condense, the presence of the trifunctional groups results in three-dimensionally crosslinked silicones. Their properties can be modified by attaching different organic groups to the backbone. This versatile material is responsible for at least six classes of commercially important products (some formulated). They are fluids, emulsions, compounds, lubricants, resins, and elastomers or rubbers.

One of the more common siloxane polymers is known as poly(dimethylsiloxane) or PDMS. Low molecular weight PDMS is sometimes known as VMS while PDMS encompass all non-volatile poly(dimethylsiloxanes):

- Volatile methylsiloxanes (VMS), are used to improve the performance of solvents, cleaners, and some personal care products (deodorants, antiperspirants).
- Polydimethylsiloxanes (PDMS), are used as end-use industrial materials, such as transformer fluids as process aids or surface treatments in the manufacture of textiles; papers and leather goods; and in a variety of personal care products such as shampoos, conditioners, skin creams, and detergents. Also known as dimethicone.
- In addition to PDMS, there are a variety of versatile functional siloxanes. These polymers contain organic functionality which enhances the benefits of standard PDMS.

The chemical structure of silane and silicone is shown in Fig. 71.1 (Wacker 1999).

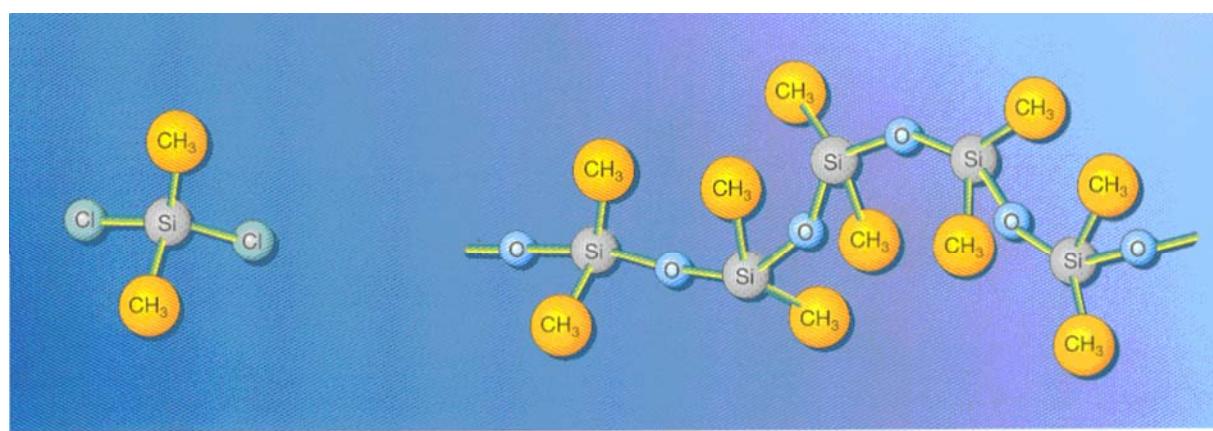


Fig. 71.1 Chemical structure of silane and silicone (Wacker 1999)

Nearly all silicone products are derived from the following three types of raw materials. Further information about the production route is given in chapter 71.5:

- Silicone fluids
- Silicone rubbers
- Silicone resins

71.4 Use of Silicone Products

The total global production of final silicone products in 2001 was almost 700 thousand tonnes (Boustead 2002). One can find specially modified silicones used in a great diversity of applications in almost every sector of industry, e.g. from construction (20%), textiles (10%), automotive (12%), paper (7%), pharmaceuticals and cosmetics to electronics (10%), optics, ceramics and biotechnology (known market shares from Boustead 2002). Silicones are manufactured as liquids, resins, reactive polymers and rubbers. They can be processed into end products as diverse as elastomers, sealants, lubricants, release agents, antifoam agents, water repellents and coatings, to list only a few of the many applications (Wacker 1999).

The most important producers are Dow Corning, GE Silicones, Rhodia Silicones, Shin-Etsu Silicones and Wacker Silicones (Boustead 2002).

Wacker Silicones was one of the first companies to introduce silicone sealants. The company is with 3,000 different silicone products one of the world's leading silicone manufacturers. Wacker Silicones is also Europe's leading silicone sealant manufacturer with an average annual output of 40,000 tonnes. All key components for silicone sealants are produced by the company (Wacker 1999).

Another important producer is (Dow Corning 2002). The company is headquartered in Midland, Michigan and employs more than 7,500 people globally at 40 manufacturing and service locations worldwide. Dow Corning makes products that fall into the basic categories described before.

71.5 System Characterisation

Fig. 71.2 shows the schematic diagram of silicone manufacturing. The basic liquid methyl chlorosilanes are produced by reacting silicon with gaseous methyl chloride. The silanes are converted in complex processes into silicone fluids, rubbers and resins. These three classes of products are themselves raw materials for other silicone products, such as greases, release agents, anti-foams, paint additives, paper coating agents, as well as for water repellents and hot and cold curing rubber (Wacker 1999).

There are two products of interest for which unit process data shall be investigated. Silicone rubber is the basic product for the production of tubes which can be used as pipes for hot water for the production of solar absorbers. Silicone sealants are a common product used in the building industry e.g. for fixing window glasses to the frame. They are also used for the manufacturing of solar collectors. Further information for these two products is given in the following subchapters.

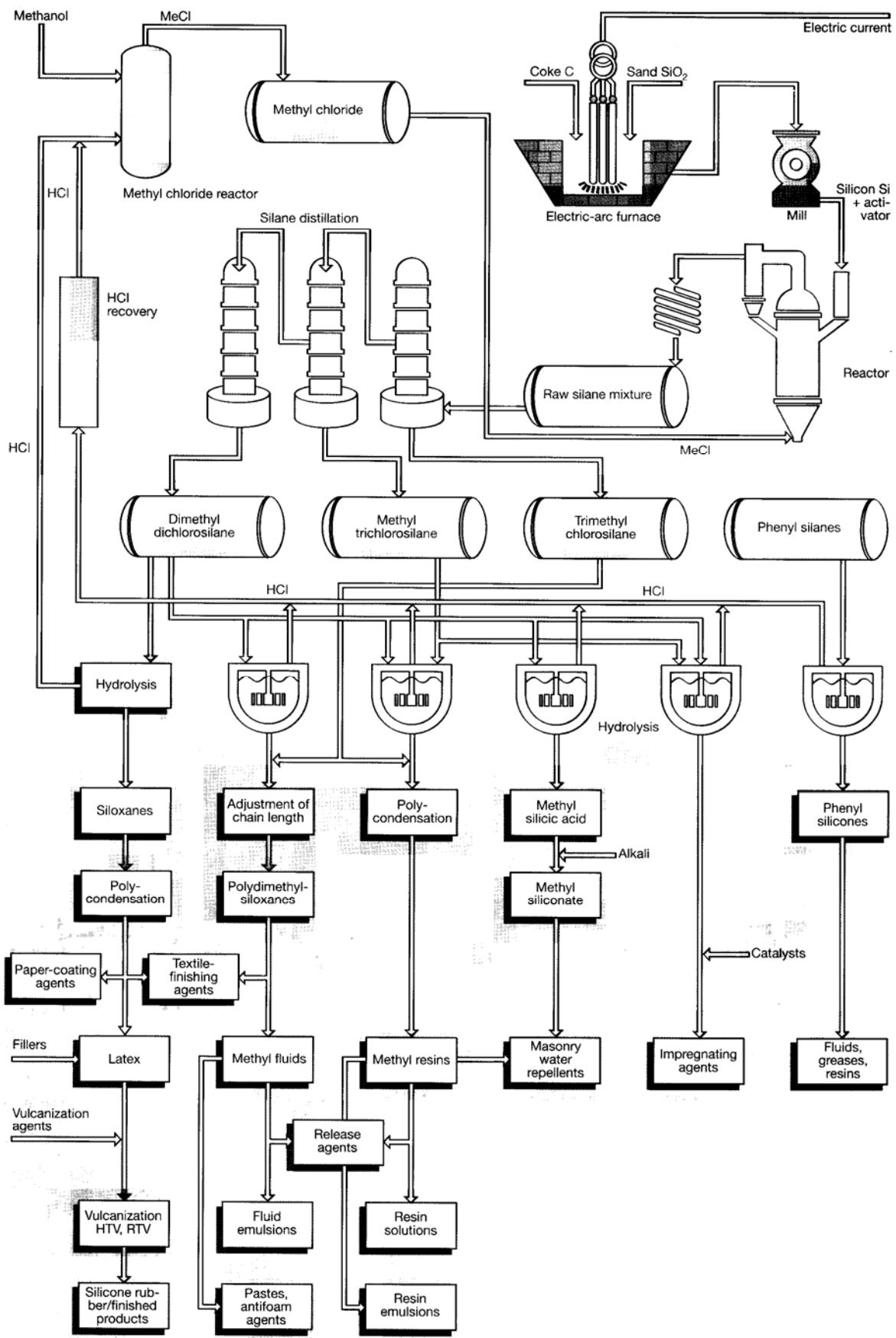


Fig. 71.2 Schematic diagram of silicone manufacture at (Wacker 1999)

71.5.1 Silicone Rubber

The basic material for silicone rubber produced in the silicone factory is HTV (High Temperature Vulcanising) rubber. The rubbers are based on high-molecular-weight polydiorganosiloxanes and reinforcing fillers. Silicone Rubber is easily extruded to make tubing, rods, gaskets, seals, wire insulation and even pre-forms used for compression moulding. Although the procedure for extruding silicone rubber is similar to other common elastomers, there are some important differences (Dow Corning 2002).

Silicone rubbers are processed on equipment normally used in the rubber industry such as moulding presses, automatic injection moulding machines, extruders and calendars. The products are vulcanised using organic peroxides (free-radical crosslinking) or functional siloxanes in conjunction with metal catalysts (addition curing) at low or high temperatures (Wacker 1999).

Extrusion should take place at room temperatures, with peak temperatures below 54°C. Higher temperatures may produce scorching and/or loss of the vulcanising agent. Generally, there is some expansion after the elastomer leaves the die.

A roller feed, with the rubber supplied from a hat or coil, ensures a more uniform extrusion than hand feed. Hot air, hot liquid or steam vulcanisation as well as autoclaving and oven curing can complete the curing of extruded silicone rubber.

71.5.2 Sealants

In a broad spectrum of applications, gluing and sealing remain the preferred methods of bonding. Many different branches of industry use adhesives and sealants made from silicon.

Silicone weatherproofing sealants minimize nature's toll on building envelopes. Silicones are virtually unaffected by sunlight, ozone, rain, snow or temperature extremes. They stay flexible and maintain adhesion even while being stretched or compressed. The sealants won't chalk, crack or split. They have a life expectancy of 20 years or more of leak-free service. They are available in an array of colours.

Sealants belong to the category of RTV-1 (Room Temperature Vulcanising, 1-component) rubbers. They are ready-to-use products which are free-flowing or paste-like in consistency. They react with atmospheric humidity to form flexible rubbers. RTV-1 silicone rubbers consist of polydimethylsiloxanes, crosslinking agents, fillers and, in some cases, solvents and additives. Basic silicone formulations of varying modules for sealants are shown in Tab. 71.1. The four sealants shown use different cure mechanisms resulting in different degrees of modules.

Some primers used for silicone sealants might cause allergic reaction due to skin contact. Solvent for the primers are emitted during hardening.

Tab. 71.1 Basic silicone formulations of varying modules (Amstock 2001:13.24)

<i>Raw materials</i>	<i>Percentage</i>			
	<i>High modulus acetoxy</i>	<i>Medium modulus oxime</i>	<i>Medium modulus oxime</i>	<i>Low modulus aminoxy siloxane</i>
Silanol polymer	80-85%	80-85%	60-80%	46.0%
Fumed silica (treated and/or untreated)	6-10%	5-10%	2-6%	—
Acetoxy cross-linker	5-7%	—	—	—
Tin catalyst	0.05-0.1%	0.05-0.1%	0.05-0.1%	—
Oxime cross-linker	—	5-7%	5-7%	—
Calcium-carbonate	—	—	20-30%	50.3%
N-methylacetamide chain extender	—	—	—	3.0%
Amino siloxane cross-linker	—	—	—	—
Silicone plasticizer	—	—	5-20%	—
Aminoxy siloxane cross-linker	—	—	—	0.7%

71.6 Life Cycle Inventories

Life cycle inventory data for specific silicone products, i.e. rubber tubes and sealants, or product groups have been investigated according to the APME methodology by the silicone industry (Boustead 2002). The production of siloxane, sealants and silicone oil is investigated in average life cycle inventories for the major producers. Intermediate results of this research show that the major energy use (ca. 50%) is the production of raw silicone. Only a small part of the cumulative energy demand is under direct influence of the producers. But, until now details are not available.²

The producers produce a range of thousands of different products in interlinked processes. It was not possible to figure out the environmental loads for a specific product. Thus the unit process raw data are investigated for an average silicone product in plants manufacturing the raw materials of interest. The inventory is based on data provided in environmental reports by an important producer (Wacker 1998; 2000a; 2000b; 2002a; 2002b).

Environmental data were available for two out of the three important manufacturing plants. This chapter gives first a short description of these plants. Further on life cycle inventory data are elaborated for the production of average silicone products.

Data for other producers were not available. The Dow Corning Responsible Care Report 2000 (Dow Corning 2002) does not show any quantitative information for the resources used and emissions caused.

Further information about environmental aspects of organosilicone materials have been published by (Chandra 1997). But this book shows no emission values of hazardous substances related to the production of silicone products.

² "I regret that the full report data is not available to third parties, following a decision by the CES Steering Committee.", Michel De Poortere, CES, Personal communication 1.2003.

71.6.1 Nünchritz, Germany

On October 1, 1998, Wacker took over the Nünchritz plant, which did belong to Hüls AG since 1991. The heart of this silicones site is the monomer complex facility and their various distillation columns. The precursor complex is where the starting materials for silicones are produced, namely methylchlorosilanes, trichlorosilanes and tetrachlorosilanes. The Nünchritz plant has been a chemicals site since 1900. It is located 50 km northwest of Dresden. The area is about 1,300,000 m².

The major product lines are chlorosilanes, polydimethylsiloxane, RTV-1 silicone rubber sealants and silicic acid esters. Other products, manufactured in lower volumes, are low, medium and high-viscosity silicone fluids, emulsions and antifoam agents, hydrogen-containing silicone fluids and polyethersiloxanes (Wacker 1999).

71.6.2 Burghausen, Germany

The Burghausen plant, founded in 1914, is the most important production site operated by Wacker and is also the largest chemical site in Bavaria. The Burghausen plant is located 110 km east of Munich. It covers an area of 2,400,000 m² with approx. 150 factories. Three divisions are based at the Burghausen site:

Wacker SILTRONIC - ranks among the world's leading producers of hyperpure silicon for the semiconductor industry.

Wacker SILICONES - is one of the world's top silicone producers. Its portfolio of over 2,000 products includes silicone fluids and resins, silicone rubber, silanes and fumed silica.

Wacker SPECIALTIES - is a world leader in the production and development of functional polymers for coatings, paints and construction applications; catalysts and industrial salt; and chemically and biotechnically produced building blocks for syntheses.

71.6.3 Peschiera-Borromeo, Italy

Although Wacker-Chemie Italia (WCI) was founded in 1982, it only became a production site in 1991. At first, WCI concentrated on RTV-1 silicone rubber production (cartridges and drums). At that time, HTV silicone rubber was still being produced by Silmix. Wacker-Chemie Italia stepped up HTV silicone rubber production in 1998.

Within the Wacker Group, WCI ranks behind Burghausen as the second largest HTV site. It supplies HTV silicone rubber for cables and seals to Spain, Sweden, Norway, Denmark, Finland and Great Britain. With an annual output of 13-15 million cartridges, WCI is Wacker's largest RTV-1 production facility. Another 4,200-5,000 metric tons of RTV-1 silicone rubber are shipped to customers throughout Europe and various Asian countries.

The production plant is located in Peschiera-Borromeo, ca. 5 km south-east of Milan. It covers an area of 23,000 m². There are approx. 130 employees.

71.6.4 Life Cycle Inventory for average Silicone Products

The inventory has been calculated as the weighted mean (sum of annual exchange divided through sum of annual output) of two production facilities which produce both a range of different products (Tab. 71.2). Environmental reports were available with data for the years 1999 and 2001 (Wacker 2000a; 2000b; 2002a; 2002b). The latest data for the plant in Nünchritz are not detailed enough. Thus the inventory is calculated with the average data for Burghausen for 1999 and 2001 and for Nünchritz only with data for 1999. The unit process raw data and data quality indicators for silicone products are shown in Tab. 71.3.

As the plant in Burghausen produces the bulk of products, data for this plant are much more important for the inventory. The amount of products produced in Nünchritz was not known. It has been calculated from the amount of raw materials used minus the amount of wastes produced. Some other figures for this plant had partly to be taken from graphics. Thus they have a high range of uncertainty.

For the Burghausen plant only the total amount of products, but not the share of different product groups was known. This plant produces about 1Mio. tonnes of products out of a little bit more than 3Mio. tonnes produced within the whole company. For that about 751000t of raw materials and 269000 tonnes of water have been used. The share of some raw materials, which have not been specified for this plant, has been calculated with the distribution found for the Nünchritz plant.

A part of the used electricity in Burghausen is produced by an own hydropower plant. Emissions of some metals from the Burghausen plant have only been reported for 1997 and not for 1999. The amount of zinc released has increased between 1994-1997 while copper emissions have been reduced and other emissions stayed stable. It is not clear if they have been fully avoided in the meantime. Figures for 1997 are used in the inventory.

Tab. 71.2 Data (total and per kg) of the years 1999 and 2001 from environmental reports for two production plants (Wacker 1998; 2000a; 2000b; 2002b).

Name	Unit	Wacker, Burghausen, 2001	Wacker, Burghausen , 2001	Wacker, Burghausen, 1999	Wacker, Burghausen , 1999	Share of Raw Materials in Nünchritz	Wacker, Nünchritz, 1999	Wacker, Nünchritz, 1999
Location		DE	DE	DE	DE	DE	DE	DE
Infrastructure	0	0	0	0	0	0	0	0
Process	kg	a	kg	a	%	kg	a	
Unit								
silicone product, at plant	kg	1.00E+0	7.45E+8	1.00E+0	1.04E+9		1.00E+0	3.92E+7
Water, cooling, unspecified natural origin	m3	2.76E-1	2.06E+8	2.31E-1	2.39E+8		-	
Water, well, in ground	m3	-	-	-	-		6.38E-2	2.50E+6
natural gas, burned in industrial furnace low-NOx >100kW	MJ	1.66E+1	1.23E+10	8.08E+0	8.37E+9		1.53E+1	6.00E+8
natural gas, burned in gas turbine	MJ	-	-	1.06E+0	1.10E+9		-	
electricity, medium voltage, production UCTE, at grid	kWh	-	-	9.25E-1	9.59E+8		9.92E-1	3.89E+7
electricity, hydropower, at power plant	kWh	3.62E-1	2.70E+8	2.60E-1	2.70E+8		-	
heavy fuel oil, burned in industrial furnace 1MW, non-modulating	MJ	4.33E-2	3.23E+7	2.44E-2	2.53E+7	3.79E+7	8.29E+0	3.25E+8
chemicals organic, at plant	kg	4.56E-2	3.39E+7	2.39E-2	2.48E+7	16.4%	1.58E-1	6.20E+6
copper, at regional storage	kg	1.50E-3	1.12E+6	7.86E-4	8.15E+5	0.5%	5.21E-3	2.04E+5
cyclohexanol, at plant	kg	1.03E-5	7.65E+3	5.40E-6	5.59E+3	0.0%	3.57E-5	1.40E+3
ethylene, average, at plant	kg	1.36E-1	1.01E+8	1.94E-1	2.01E+8		1.13E-1	4.44E+6
fluosilicic acid, 22% in H2O, at plant	kg	5.47E-3	4.07E+6	2.87E-3	2.98E+6	2.0%	1.90E-2	7.45E+5
isopropanol, at plant	kg	5.36E-4	3.99E+5	2.81E-4	2.92E+5	0.2%	1.86E-3	7.30E+4
quicklime, milled, packed, at plant	kg	3.32E-2	2.47E+7	1.74E-2	1.80E+7	11.9%	1.15E-1	4.52E+6
methanol, at regional storage	kg	8.30E-2	8.60E+7	8.30E-2	8.60E+7		9.33E-2	3.66E+6
methylchloride, at regional storage	kg	1.75E-1	1.30E+8	9.17E-2	9.50E+7	62.8%	6.07E-1	2.38E+7
MG-silicon, at plant	kg	1.03E-1	7.70E+7	5.40E-2	5.59E+7		3.36E-1	1.32E+7
Polyethylene, HDPE, granulate, at plant	kg	1.47E-3	1.09E+6	7.71E-4	7.99E+5	0.5%	5.10E-3	2.00E+5
silicon tetrachloride, at plant	kg	1.39E-3	1.03E+6	7.29E-4	7.55E+5	0.5%	4.82E-3	1.89E+5
sodium chloride, powder, at plant	kg	8.73E-2	6.50E+7	2.48E-1	2.57E+8		1.07E-3	4.20E+4
sodium hydroxide, 50% in H2O, production mix, at plant	kg	2.92E-3	2.18E+6	1.53E-3	1.59E+6	1.1%	1.02E-2	3.98E+5
sulphuric acid, liquid, at plant	kg	1.12E-2	8.37E+6	5.90E-3	6.11E+6	4.0%	3.91E-2	1.53E+6
tin, at regional storage	kg	8.81E-5	6.56E+4	4.63E-5	4.79E+4	0.0%	3.06E-4	1.20E+4
titanium dioxide, production mix, at plant	kg	1.47E-5	1.09E+4	7.71E-6	7.99E+3	0.0%	5.10E-5	2.00E+3
toluene, liquid, at plant	kg	1.47E-6	1.09E+3	7.71E-7	7.99E+2	0.0%	5.10E-6	2.00E+2
zinc for coating, at regional storage	kg	1.17E-5	8.75E+3	6.17E-6	6.39E+3	0.0%	4.08E-5	1.60E+3
tap water, at user	kg	2.69E-1	2.00E+8	2.60E-1	2.69E+8	100.0%	3.57E-1	1.40E+7
transport, lorry 32t	tkm	2.79E-1	2.08E+8	1.80E-1	1.87E+8		8.24E-1	3.23E+7
transport, freight, rail	tkm	4.32E-1	3.22E+8	4.35E-1	4.51E+8		9.06E-1	3.55E+7
silicone plant	unit	1.00E-11	7.45E-3	1.00E-11	1.04E-2		1.00E-11	3.92E-4
disposal, hazardous waste, 25% water, to hazardous waste incineration	kg	2.68E-2	2.00E+7	4.26E-2	4.41E+7		5.10E-2	2.00E+6
disposal, municipal solid waste, 22.9% water, to municipal incineration	kg	3.61E-2	2.69E+7	8.32E-3	8.62E+6		5.10E-2	2.00E+6
disposal, municipal solid waste, 22.9% water, to sanitary landfill	kg	-	-	-	-		1.02E-1	4.00E+6
Heat, waste	MJ	1.30E+0	9.71E+8	4.27E+0	4.42E+9		3.57E+0	1.40E+8
Halogenated hydrocarbons, chlorinated	kg	1.07E-5	8.00E+3	3.28E-5	3.40E+4		-	
Hydrocarbons, aliphatic, alkanes, unspecified	kg	4.12E-4	3.07E+5	3.65E-4	3.78E+5		-	
Hydrogen chloride	kg	4.30E-5	3.20E+4	3.57E-5	3.70E+4		-	
Particulates, > 2.5 um, and < 10um	kg	6.85E-5	5.10E+4	7.63E-5	7.90E+4		-	
Silicon	kg	1.34E-4	1.00E+5	5.79E-5	6.00E+4		-	
AOX, Adsorbable Organic Halogen as Cl	kg	1.21E-5	9.00E+3	9.65E-6	1.00E+4		1.28E-5	5.00E+2
BOD5, Biological Oxygen Demand	kg	1.96E-4	1.46E+5	-	-		-	
Cadmium, ion	kg	na	na	1.74E-8	1.80E+1		2.55E-5	1.00E+3
Chloride	kg	3.45E-2	2.57E+7	3.27E-2	3.39E+7		1.53E-1	6.00E+6
Chromium, ion	kg	na	na	8.17E-7	8.46E+2		-	
COD, Chemical Oxygen Demand	kg	1.94E-3	1.44E+6	-	-		2.55E-3	1.00E+5
Copper, ion	kg	9.81E-8	7.30E+1	1.16E-6	1.20E+3		-	
Fluoride	kg	na	na	3.85E-5	3.99E+4		-	
Lead	kg	na	na	2.11E-7	2.19E+2		-	
Mercury	kg	na	na	1.93E-9	2.00E+0		-	
Nickel, ion	kg	na	na	8.28E-7	8.58E+2		-	
Nitrogen	kg	1.99E-4	1.48E+5	2.92E-4	3.02E+5		1.02E-3	4.00E+4
Phosphate	kg	2.69E-6	2.00E+3	5.79E-6	6.00E+3		-	
Phosphorus	kg	na	na	-	-		1.28E-5	5.00E+2
Sulfate	kg	na	na	-	-		5.10E-3	2.00E+5
Sodium, ion	kg	3.24E-2	2.41E+7	2.51E-2	2.60E+7		-	
Zinc, ion	kg	1.88E-6	1.40E+3	1.93E-6	2.00E+3		-	
Iron, ion	kg	5.37E-6	4.00E+3	6.76E-6	7.00E+3		-	
TOC, Total Organic Carbon	kg	8.72E-4	6.49E+5	6.56E-4	6.80E+5		-	

a annual

Tab. 71.3 Unit process raw data and data quality indicators for silicone products. Average of data for two production plants

	Name	Location	InfrastructureProcess	Unit	silicone product, at plant RER 0 kg	Uncertai nStandar dDeviant	GeneralComment	
							chirPro	Unit
product	silicone product, at plant	RER	0	kg	1.00E+0			
resource, in water	Water, cooling, unspecified natural origin	-	-	m3	2.39E-1	1	1.07 (1,2,1,1,1,3); Internal production	
	Water, well, in ground	-	-	m3	2.69E-3	1	1.07 (1,2,1,1,1,3); Environmental report	
technosphere	natural gas, burned in industrial furnace low-NOx >100kW	RER	0	MJ	1.18E+1	1	1.07 (1,2,1,1,1,3); Environmental report	
	natural gas, burned in gas turbine	DE	0	MJ	5.93E-1	1	1.07 (1,2,1,1,1,3); Electricity production	
	electricity, medium voltage, production UCTE, at grid	UCTE	0	kWh	5.58E-1	1	1.07 (1,2,1,1,1,3); Environmental report	
	electricity, hydropower, at power plant	DE	0	kWh	2.90E-1	1	1.07 (1,2,1,1,1,3); Internal production	
	heavy fuel oil, burned in industrial furnace 1MW, non-modulating	RER	0	MJ	3.81E-1	1	1.07 (1,2,1,1,1,3); Environmental report	
	chemicals organic, at plant	GLO	0	kg	3.83E-2	1	1.07 (1,2,1,1,1,3); Environmental report, different special chemicals	
	copper, at regional storage	RER	0	kg	1.26E-3	1	1.07 (1,2,1,1,1,3); Environmental report	
	cyclohexanol, at plant	RER	0	kg	8.63E-6	1	1.07 (1,2,1,1,1,3); Environmental report	
	ethylene, average, at plant	RER	0	kg	1.67E-1	1	1.07 (1,2,1,1,1,3); Environmental report, ethanol used in Nünchritz	
	fluosilicic acid, 22% in H2O, at plant	RER	0	kg	4.59E-3	1	1.07 (1,2,1,1,1,3); Silicic acid	
	isopropanol, at plant	RER	0	kg	4.50E-4	1	3.00 (1,2,1,1,1,3); Environmental report	
	quicklime, milled, packed, at plant	CH	0	kg	2.78E-2	1	1.07 (1,2,1,1,1,3); Environmental report	
	methanol, at regional storage	CH	0	kg	9.65E-2	1	1.07 (1,2,1,1,1,3); Environmental report	
	methylchloride, at regional storage	CH	0	kg	1.47E-1	1	1.07 (1,2,1,1,1,3); Environmental report	
	MG-silicon, at plant	NO	0	kg	8.57E-2	1	1.07 (1,2,1,1,1,3); Raw silicon	
	Polyethylene, HDPE, granulate, at plant	RER	0	kg	1.23E-3	1	1.07 (1,2,1,1,1,3); Environmental report	
	silicon tetrachloride, at plant	DE	0	kg	1.17E-3	1	1.07 (1,2,1,1,1,3); Environmental report	
	sodium chloride, powder, at plant	RER	0	kg	1.73E-1	1	1.07 (1,2,1,1,1,3); Environmental report	
	sodium hydroxide, 50% in H2O, production mix, at plant	RER	0	kg	2.45E-3	1	1.07 (1,2,1,1,1,3); Environmental report	
	sulphuric acid, liquid, at plant	RER	0	kg	9.44E-3	1	1.07 (1,2,1,1,1,3); Environmental report	
	tin, at regional storage	RER	0	kg	7.40E-5	1	1.07 (1,2,1,1,1,3); Environmental report	
	titanium dioxide, production mix, at plant	RER	0	kg	1.23E-5	1	1.07 (1,2,1,1,1,3); Environmental report	
	toluene, liquid, at plant	RER	0	kg	1.23E-6	1	1.07 (1,2,1,1,1,3); Environmental report	
	zinc, primary, at regional storage	RER	0	kg	9.86E-6	1	1.07 (1,2,1,1,1,3); Dibutylzinnacetat	
	tap water, at user	RER	0	kg	2.67E-1	1	1.07 (1,2,1,1,1,3); Environmental report	
	transport, lorry >16t, fleet average	RER	0	tkm	2.47E-1	1	2.09 (4,5,na,na,na,na); Standard distance 100km, MG-Si 2000km	
	transport, freight, rail	RER	0	tkm	4.54E-1	1	2.09 (4,5,na,na,na,na); Standard distance 600km	
	silicone plant	RER	1	unit	1.00E-11	1	3.00 (1,2,1,1,1,3); Environmental report	
	disposal, hazardous waste, 25% water, to hazardous waste incineration	CH	0	kg	3.66E-2	1	1.07 (1,2,1,1,1,3); Internal disposal	
	disposal, municipal solid waste, 22.9% water, to municipal incineration	CH	0	kg	2.12E-2	1	1.07 (1,2,1,1,1,3); Environmental report	
	disposal, municipal solid waste, 22.9% water, to sanitary landfill	CH	0	kg	4.30E-3	1	1.07 (1,2,1,1,1,3); Environmental report	
emission air, high population density	Heat, waste	-	-	MJ	3.05E+0	1	1.07 (1,2,1,1,1,3); Calculation	
	Halogenated hydrocarbons, chlorinated	-	-	kg	2.26E-5	1	1.51 (1,2,1,1,1,3); Environmental report	
	Hydrocarbons, aliphatic, alkanes, unspecified	-	-	kg	3.69E-4	1	1.51 (1,2,1,1,1,3); Environmental report	
	Hydrogen chloride	-	-	kg	3.71E-5	1	1.51 (1,2,1,1,1,3); volatile anorganic compounds	
	Particulates, > 2.5 um, and <10um	-	-	kg	6.99E-5	1	3.00 (1,2,1,1,1,3); Dust	
Emission water, river	Silicon	-	-	kg	8.61E-5	1	1.51 (1,2,1,1,1,3); Org. Si-compounds	
	AOX, Adsorbable Organic Halogen as Cl	-	-	kg	1.08E-5	1	3.00 (1,2,1,1,1,3); Environmental report	
	BOD5, Biological Oxygen Demand	-	-	kg	7.85E-5	1	1.51 (1,2,1,1,1,3); Environmental report	
	Cadmium, ion	-	-	kg	9.47E-7	1	5.77 (1,2,2,1,5,3); Environmental report, 1997, heavy metals	
	Chloride	-	-	kg	3.85E-2	1	1.51 (1,2,1,1,1,3); Environmental report	
	Chromium, ion	-	-	kg	7.87E-7	1	5.00 (1,2,1,1,1,3); Environmental report, 1997	
	COD, Chemical Oxygen Demand	-	-	kg	8.83E-4	1	1.51 (1,2,1,1,1,3); Environmental report	
	Copper, ion	-	-	kg	6.85E-7	1	5.01 (1,2,2,1,1,3); Environmental report, 1997	
	Fluoride	-	-	kg	3.71E-5	1	1.51 (1,2,2,1,1,3); Environmental report, 1997	
	Lead	-	-	kg	2.04E-7	1	5.01 (1,2,2,1,1,3); Environmental report, 1997	
	Mercury	-	-	kg	1.86E-9	1	5.01 (1,2,2,1,1,3); Environmental report, 1997	
	Nickel, ion	-	-	kg	7.98E-7	1	5.01 (1,2,2,1,1,3); Environmental report, 1997	
	Nitrogen	-	-	kg	2.85E-4	1	1.51 (1,2,1,1,1,3); Environmental report	
	Phosphate	-	-	kg	4.30E-6	1	1.51 (1,2,1,1,1,3); Environmental report	
	Phosphorus	-	-	kg	4.65E-7	1	1.51 (1,2,1,1,1,3); Environmental report	
	Sulfate	-	-	kg	1.86E-4	1	1.51 (1,2,1,1,1,3); Environmental report	
	Sodium, ion	-	-	kg	2.70E-2	1	1.51 (1,2,1,1,1,3); Environmental report	
	Zinc, ion	-	-	kg	1.83E-6	1	5.00 (1,2,1,1,1,3); Environmental report	
	Iron, ion	-	-	kg	5.92E-6	1	5.00 (1,2,1,1,1,3); Environmental report	
	TOC, Total Organic Carbon	-	-	kg	7.15E-4	1	1.51 (1,2,1,1,1,3); Environmental report	
	DOC, Dissolved Organic Carbon	-	-	kg	7.15E-4	1	1.78 (5,2,1,1,1,3); Rough estimation with TOC	

71.6.5 Life Cycle Inventory for the Silicone Manufacturing Plant

The unit process raw data for the manufacturing plant in Tab. 71.4 have been assessed with data provided by Wacker (2000a; 2000b; 2002a; 2002b) for two production plants. The data have been normalized for a production capacity of 1 000 000t/a. As silicone is produced at long time chemical production places a life time of 100a has been assumed for the land transformation. The infrastructure for the chemical processing units has been estimated roughly with generic data and doubled because of the shorter life time of 50a.

Tab. 71.4 Unit process raw data and data quality indicators for the silicone manufacturing plant with a production capacity of 1 000 000t/a and a life time of 100 years

	Name Location InfrastructureProcess Unit	Locati on	infrast ructur e	Unit	silic one plant RER 1 unit	uncer tai nty	ardDe viation	GeneralComment	Wacker, Burghausen	Wacker, Nünchritz
									DE	DE
product	silicone plant	RER	1	unit	1.00E+0				8.90E+8	3.92E+7
technosphere	building, hall	CH	1	m2	2.28E+6	1	3.00	(1,2,1,1,1,3); Calculation for 100a, approx. 150 factories	4.10E+5	6.50E+5
	facilities, chemical production	RER	1	kg	3.20E+7	1	3.90	(5,na,1,1,5,na); Rough estimation, doubled inventory for life time of 100a.		
	pipeline, crude oil, onshore	RER	1	km	2.54E+2	1	3.00	(1,2,1,1,1,3); Calculation for 100a, approx. 150 factories	1.13E+2	
	pipeline, natural gas, low pressure distribution network	CH	1	km	1.62E+2	1	3.00	(1,2,1,1,1,3); Calculation for 100a, approx. 150 factories	7.20E+1	
	railway track	CH	1	ma	6.29E+4	1	3.00	(1,2,1,1,1,3); Calculation for 100a, approx. 150 factories	2.80E+4	
	disposal, railway track	CH	1	ma	6.29E+4	1	3.00	(1,2,1,1,1,3); Calculation for 100a, approx. 150 factories		
resource, land	disposal, facilities, chemical production	RER	0	kg	3.20E+7	1	3.90	(5,na,1,1,5,na); Rough estimation		
	Occupation, industrial area, built up	-	-	m2a	1.14E+8	1	1.51	(1,2,1,1,1,3); 100a occupation	4.10E+7	6.50E+7
	Occupation, industrial area, vegetation	-	-	m2a	1.60E+8	1	1.51	(1,2,1,1,1,3); 100a occupation	8.40E+7	6.50E+7
	Occupation, traffic area, road network	-	-	m2a	5.06E+7	1	1.51	(1,2,1,1,1,3); 100a occupation	4.70E+7	-
	Occupation, dump site	-	-	m2a	2.15E+7	1	1.51	(1,2,1,1,1,3); 100a occupation	2.00E+7	-
	Transformation, from unknown	-	-	m2	3.46E+6	1	2.00	(1,2,1,1,1,3); Environmental report	1.92E+6	1.30E+6
	Transformation, to industrial area, built up	-	-	m2	1.14E+6	1	2.00	(1,2,1,1,1,3); Environmental report	4.10E+5	6.50E+5
	Transformation, to industrial area, vegetation	-	-	m2	1.60E+6	1	2.00	(1,2,1,1,1,3); Environmental report	8.40E+5	6.50E+5
	Transformation, to traffic area, road network	-	-	m2	5.06E+5	1	2.00	(1,2,1,1,1,3); Environmental report	4.70E+5	-
	Transformation, to dump site, residual material landfill	-	-	m2	2.15E+5	1	2.00	(1,2,1,1,1,3); Environmental report	2.00E+5	-

71.7 Data Quality Considerations

The simplified approach with a pedigree matrix has been used for calculating the standard deviation. The data quality for the unit process of an average silicone product is good. But there may be large differences between different products. Thus in case this raw materials turns out to be important in a life cycle assessment a more detailed investigation of the specific product has to be made. Some silicone products need further processing before the end use product can be sold. Silicone tubes, for example, are made for example from silicone rubber. The production of the tubes needs further chemicals and energy which is not included in the unit process raw data shown here.

71.8 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

71.9 Conclusions

The inventory for average silicone products is meant to be used as a background information in inventories where these products make only a small part of the inputs. This inventory can give an approximation of the environmental impacts due to the production of these raw materials. For a detailed analysis and the direct comparison of a specific silicone product with another material further investigation would be necessary. Especially for the specific products shown in Fig. 71.2 this inventory underestimates the environmental impacts.

Abbreviations

a	annual
HTV	High Temperature Vulcanising rubbers. Used for extruded articles, seals, cable insulation, tubes, profiles, etc. Example: liquid silicone rubber.
PDMS	poly(dimethylsiloxane)
RTV-1	Room Temperature Vulcanising, 1-component. Ready-for-use, one-pack compound. Vulcanizes in contact with atmospheric moisture. For seals, sealants, sealants and adhesives, etc.
RTV-2	Room-Temperature Vulcanising on addition of a second component, e.g. crosslinking agent. Used for mold-making, insulation material, embedding material in the electrical and electronics industries. Sub-divided into addition-crosslinking and condensation-crosslinking silicone rubber.
STC	silicon tetrachloride
VMS	Volatile methylsiloxanes

Appendices: EcoSpold Meta Information

ReferenceFunction	401 Name	silicone product, at plant	silicone plant
Geography	662 Location	RER	RER
ReferenceFunction	493 InfrastructureProcess	0	1
ReferenceFunction	403 Unit	kg	unit
DataSetInformation	201 Type	1	1
	202 Version	1.0	1.0
	203 energyValues	0	0
	205 LanguageCode	en	en
	206 LocalLanguageCode	de	de
DataEntryBy	302 Person	41	41
	304 QualityNetwork	1	1
ReferenceFunction	400 DataSetRelatesToProduct	1	1
	402 IncludedProcesses	Gate to gate inventory for the production of average silicon products.	Inventory for the production plant including land use, machinery and buildings.
	404 Amount	1	1
	490 LocalName	Silikonprodukt, ab Werk	Silikonfabrik
	491 Synonyms	chlorosilanes // polydimethylsiloxane // RTV-1 silicone rubber sealants // silicic acid esters // hyperpure silicon // silicones // silanes // silica // organics // cyclodextrins // vinyl polymers	
	492 GeneralComment	Average of about 2000 products. The inventory has been calculated as a weighted mean of two production facilities which produce both a range of different products.	Average of two plants. Chemical production since more than 100 years. Life time estimated to be 100a. Annual production 1 Mio. tonnes.
	494 InfrastructureIncluded		
	495 Category	chemicals	chemicals
	496 SubCategory	inorganics	inorganics
	497 LocalCategory	Chemikalien	Chemikalien
	498 LocalSubCategory	Anorganika	Anorganika
	499 Formula		
	501 StatisticalClassification		
	502 CASNumber		
TimePeriod	601 StartDate	1997	1999
	602 EndDate	2001	2001
	603 DataValidForEntirePeriod	1	1
	611 OtherPeriodText	Reporting time of environmental reports.	Reporting time of environmental reports.
Geography	663 Text	Production plant in DE. No data for IT, US, IN and other locations.	Production plant in DE.
Technology	692 Text	Integrated chemical processing facilities with 150 different factories, e.g. electric furnace, silane distillation, hydrolysis, storage tanks, etc.	Chemical production facility.
Representativeness	722 Percent		
	724 ProductionVolume	About 0.7Mio. tonnes in 2000	Normalized for a production capacity of 1 000 000t/a.
	725 SamplingProcedure	Environmental reports for 2 plants.	Environmental reports and webpage.
	726 Extrapolations	Average data for a range of products	None
	727 UncertaintyAdjustments	none	none
DataGenerator AndPublication	751 Person	41	41
	756 DataPublishedIn	2	2
	757 ReferenceToPublishedSource	7	7
	758 Copyright	1	1
	759 AccessRestrictedTo	0	0
	760 CompanyCode		
	761 CountryCode		
	762 PageNumbers	chapter silicones	chapter silicones

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72 Soda and Calcium chloride

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Review: Heiko Kunst, TU Berlin

Last Changes: 2004

72.1 Introduction Soda

Soda (Ca_2CO_3 , CAS-No. 497-19-8) is the neutral sodium salt of carbonic acid. The most important chemical and physical properties are summarised here below.

Synonyms for soda: soda ash; sodium carbonate; carbonic acid disodium salt; disoda; calcined soda; Ash.

Tab. 72.1 Chemical and physical properties of soda (Chemfinder (2002)).

Property	Value	Unit	Property	Value	Unit
Molecular weight	105.9887	g mol^{-1}	Melting point	851	$^{\circ}\text{C}$
Density (at 20°C)	2.532	g cm^{-3}	Boiling point	1600	$^{\circ}\text{C}$

The following description of production technology and the use of soda are summarized from UBA (2001), Woode (1995) and Thieme (1993).

72.1.1 Reserves and Resources

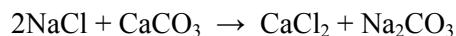
Currently 80-85 % of the world capacity is being utilised. UBA (2001) states a world annual production of soda of about 31.5 Mio tonnes for 1993, being 65% of it synthetic soda manufactured by means of the Solvay technique. UN (1995) reports a world annual production of 28.5 Mio tonnes for 1993, from which 9.3 Mio tonnes correspond to Europe and 5.1 Mio tonnes to the EU.

Soda is produced basically from ammonia, sodium chloride and calcium carbonate. Therefore, the resources available as well as the reserves are the same as for the production of the mentioned chemicals, described in the corresponding chapters.

72.1.2 Production Technologies and Use

Production technologies for soda

One of the manufacturing process in use worldwide for the production of soda is the "Solvay process" also called "ammonia process". This is the only relevant process in use in Europe. The technical manufacture of soda with the Solvay technique is effected by the conversion of sodium chloride (salt) and calcium carbonate (limestone) according to the following general equation:



Besides soda the Solvay technique also causes CaCl_2 as a by-product. The Solvay process is explained in detail in chapter 72.3.

The other relevant soda manufacturing process is the **natural ash process**. The so-called sources of natural ash are generally deposits of either Trona (sodium sesquicarbonate dihydrate) or nahcolite (sodium hydrogen carbonate), or brines containing soda or bicarbonate. These materials require to be separated from the impurities they are associated with in their deposits, and all have to be subjected to at least one calcining stage, to convert the material into sellable soda. Thus the materials require significant processing before they yield soda. This kind of process is principally used in the United States.

Besides the production by means of the Solvay technique and natural soda ash process, soda is also manufactured as a **by-product of the caprolactam production**, for example at BASF-Ludwigshafen. This kind of production is a special proceeding and it is not further considered since it represents only a little contribution to the total soda production.

Additionally, many **variants of the ammonia process** exist. One of them is the **dual process**, developed and operated in Japan. This process combines soda production with ammonium chloride production. The importance of the process in Japan is due to the high cost of imported rock salt and use of the ammonium chloride as a fertiliser. In this process ammonia is absorbed by the bicarbonate mother liquor and solid sodium chloride is added. On cooling, ammonium chloride separates and is recovered and dried. The mother liquor is recycled to the carbonation towers where sodium bicarbonate is precipitated.

Much work has been done in an attempt to develop alternatives to the conventional ammonia process, and there are many processes that can be used to form soda from salt, but none has proved commercially attractive. Amongst the processes which come nearest to commercial practicability are those where an **organic amine** has been used to replace the ammonia.

Over the years many improvements have been made in the process equipment and economics achieving much more compact and process intensive devices. Methods of converting sodium bicarbonate directly into heavy ash without the intermediate light ash stage have also been developed, although they are not applied widely. In terms of efficiency, control techniques have improved to an extent where raw materials efficiencies are very near the theoretical limits; computer control is the norm in modern plants. Heat recovery between process streams is also very extensive. Fundamental energy studies have shown that the modern plant configurations are such that energy usage can be within 2% of the theoretical optimum for the given chemistry of the particular process.

72.1.3 Use

Soda is the chemical product, which is used for the most different purposes. The predominant share is required in the glass industry, where it is used as raw material for the decomposition of sand. Another main share of soda is used in the chemical industry for the production of chemicals. In the detergent and soap industry, soda ash is used for the manufacture of detergents and for the saponification of grease. Also the paper and cellulose industry uses soda for the digestion, the neutralization, the cleaning and the leaching as well as for the recycling of wastepaper. Smaller quantities of soda are required in almost every production branch.

Soda ash is manufactured in two grades: "light ash" and "heavy ash", the difference being the much greater volume occupied by a given mass of light ash. Heavy ash, when transported in bulk, has a pouring density equal to or slightly above that of water, whereas the pouring density of light ash is only half of this value. Heavy ash is clearly the preferred form for economic transportation over long distances. For general chemicals production light ash is widely used because of its traditionally lower price, its higher rate of dissolution and reaction, and its freedom from calcium ions, which are unacceptable in certain processes, for example soap manufacture.

72.2 Introduction Calcium chloride

Calcium chloride (CaCl_2 , CAS-No. 10043-52-4) is a white, odourless extremely water soluble salt. Calcium chloride is most widely used for its de-icing and dust control abilities.

For this inventory the functional unit is 1 kg of calcium chloride (active substance). The inventory refers to commercial calcium chloride flakes (calcium chloride dihydrate) containing 77-82 wt-% calcium chloride. Some chemical and physical properties of calcium chloride used in this inventory are given in the following table.

Tab. 72.2 Chemical and physical properties of calcium chloride (Ullmann 2001)

Property	Unit	Value	Remarks
Molecular weight of anhydrous calcium chloride	g mol ⁻¹	111.0	
Specific gravity of anhydrous calcium chloride	kg m ⁻³	2200	at 25 °C
Specific gravity of calcium chloride flakes (77%)	kg m ⁻³	1920	at 25 °C

72.2.1 Reserves and Resources of material

Commercial production of calcium chloride is strongly determined by the availability of brines and the cost of the synthetic production processes (as e.g. the Solvay process). While commercial production in the U.S. is dominated by the refining of natural brine or by neutralisation of by-product hydrochloric acid with limestone, in Europe calcium chloride is produced to a large extend as a by-product from the soda ash production.

According to (Ullmann 2001) 15.48 Mt calcium chloride (as 100% CaCl₂) were produced in 1979 in Europe from the Solvay process. Since then the production capacity of the soda ash production has decreased and therefore also the production output for calcium chloride will have decreased. There were no actual numbers for the present production available.

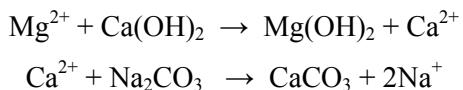
72.2.2 Use of material / product

The largest market for calcium chloride is the de-icing of roads. For this application the calcium chloride is used in form of flakes with at least 77 wt-% calcium chloride. There are no special requirements on the purity of the product for this application. Standards secure that the amount of harmful impurities is limited.

According to (ChemExpo 1999) in the U.S. 35% of the calcium chloride was used for de-icing, 20% for road stabilisation and dust control, 20% for industrial processing, 10% for oil and gas well fluids, 10% for concrete and 5% for miscellaneous uses (values for year 2000). There were no data available of the use of calcium chloride in Europe or in Switzerland, but it can be assumed that road de-icing will also here be the major use of the material.

72.3 The Solvay process

The manufacture of soda by means of the Solvay process begins with the brine being led to a cleaning step, since inorganic by-materials may cause difficulties in the production process and lead to a lower quality of the final product. A typical ammonia-soda manufacturing plant is illustrated in Fig. 72.1. Mainly calcium and magnesium ions can generate carbonates during the ammonia absorption, which causes incrustations in the installations and the tubes. The cleaning is normally effected by means of the lime-soda-procedure (lime milk and soda solution are added into the brine). In this process the Mg²⁺-ion is precipitated to hydroxide and the Ca²⁺-ion to carbonate, according to the following reaction equations:

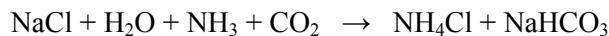


The effluents discharged by the process described above are loaded with solids. The cleaned brine is led into several gas scrubbers in countercurrent to the offgases from the absorption, the carbonisation, the filtration and the calcination. The brine recovers the ammonia and a part of the carbon dioxide contained in the off-gases.

The main absorption of the brine with ammonia takes place in the subsequent absorption step under the addition of a part of the required carbon dioxide (approximately 20 %).

NH₃-losses during the process are compensated by the help of the ammonia water receptacle. The off-gas from the absorption is led across the gas scrubber run with the brine and is then added to the exhaust gas from the calcination. The ammonia concentration of the brine amounts now to approximately 85 - 90 kg NH₃/m³. Because the reactions running during the absorption are strongly exothermic, the absorption columns are equipped with coolers.

Afterwards, the ammoniacal brine is oversaturated with carbon dioxide from the limekiln as well as from the calcination led in countercurrent and sodium bicarbonate is precipitated:



Also the carbonisation is an exothermic process, so that the cast-iron precipitation columns are equipped with tube coolers in the lower part. The off-gas from the carbonisation is washed with brine in a countercurrent and afterwards discharged into the atmosphere. As the installations of the precipitation columns including the cool tubes crust within few days due to the precipitated bicarbonate, they must be rinsed. This is effected by the help of fresh ammoniacal brine under the addition of a few carbonic acid gas, through which the incrustations are dissolved again. The precarbonized rinse brine is then led onto parallel precipitation columns, which are less crusted.

Afterwards the precipitated bicarbonate is filtered from the mother liquor by means of vacuum filters or centrifuges. Mother liquor still contained in the bicarbonate is washed off by the use of condensates from the production or by softened wash water. The wash water volume fluctuates between 0,0003 and 0.001 m³/kg soda according to the grain size of the bicarbonate. The off-gas from the filtration is washed in countercurrent with fresh brine and then discharged into the atmosphere.

The filtered raw bicarbonate is approximately composed as follows:

NaHCO ₃	75,6%
Na ₂ CO ₃	6,9%
NH ₄ HCO ₃	3,4%
NaCl + NH ₄ Cl	0,4%
H ₂ O	13,7%

The residual humidity of the raw bicarbonate influences the energy demand of the subsequent thermic decomposition to soda (calcination). The calcination generates carbon dioxide and steam:



Besides the main reaction, i.e. the generation of soda, the calcination also leads to the following parallel reactions, which generate ammonia as well as sodium chloride:



In the above described side reaction, soda is polluted with sodium chloride. From one ton of crude bicarbonate approximately 520 - 560 kg of soda are generated by calcination. The decomposition takes place above 100 °C, generally temperatures above 170 °C are used to ensure a complete reaction. The off-gas sucked from the steam heated rotatory drums contains, besides CO₂, NH₃ and H₂O, also larger quantities of dust.

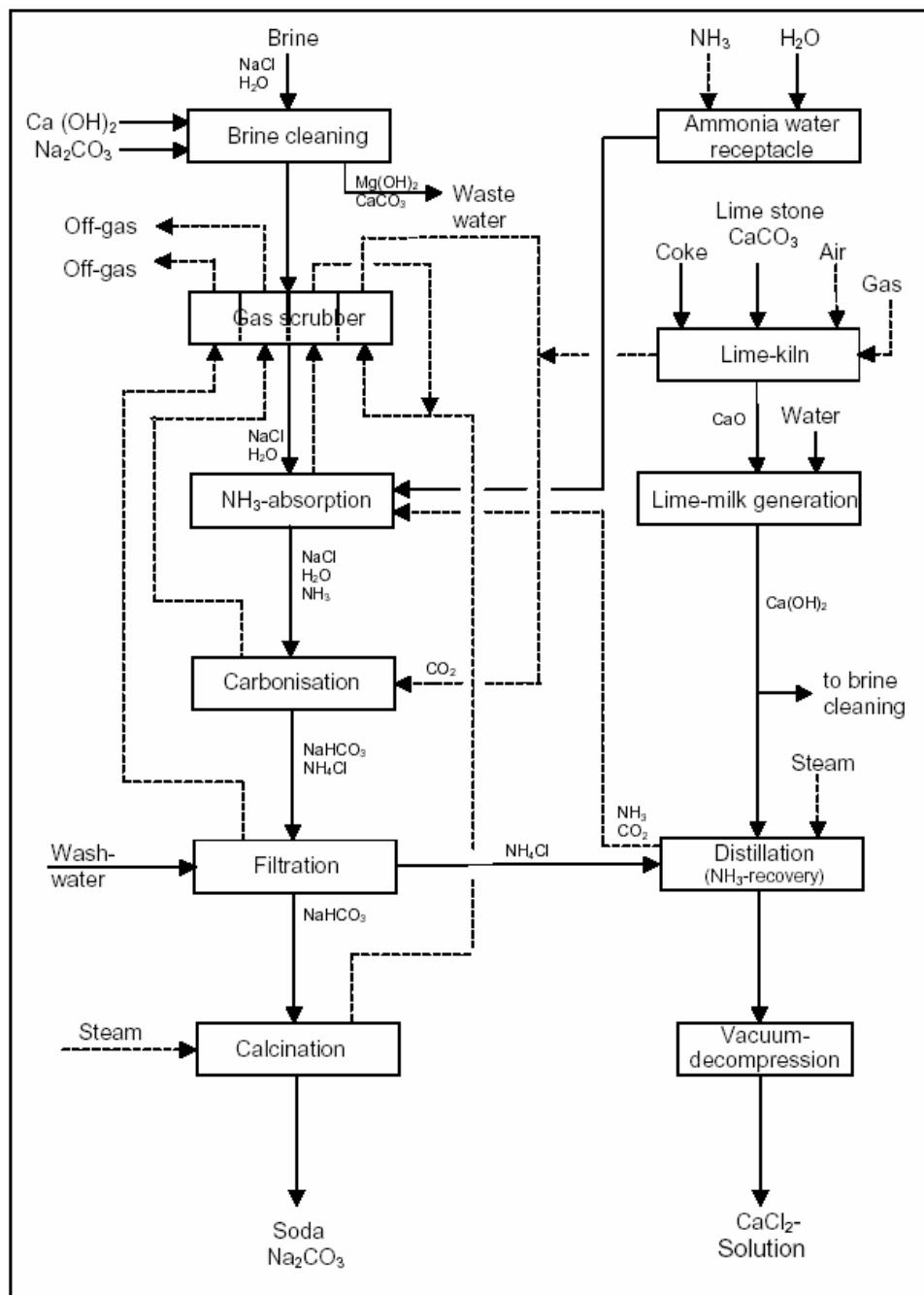
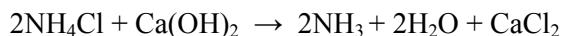


Fig. 72.1 Soda production by means of the Solvay technique (taken from Fig.1 UBA (2001))

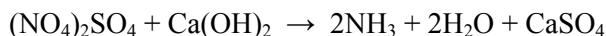
The product withdrawn from the calcination is either directly packed as "easy soda" or "light soda" with a pour weight of 0,6 - 0,7 t/m³ or it is changed to a monohydrate and then into "heavy soda" with a pour weight of 1,05 t/m³ by means of hydration and subsequent dehydration. The manufacture of soda briquettes is also possible by the addition of sodium silicate (water glass). (The mentioned bulk densities are extracted from UBA 2001; for Thieme (1993) light ash has a bulk density of 0.5 to 0.6 t/m³ and heavy ash, 1.05 to 1.15 t/m³.)

The residual ammonia in the filter lye in form of carbonate, hydrogen carbonate, sulfate and chloride is recovered by distillation and is led back to the NH₃-absorption. Consequently ammonia represents a pure support material. Merely inevitable losses are supplemented by concentrated aqueous NH₃-solutions (25%) from the ammonia receptacle.

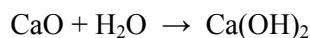
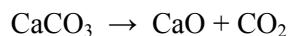
$(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 are completely decomposed already at temperatures of 85 - 90 °C and the entire carbon dioxide and a small part of the ammonia is separated from the solution. For the separation of ammonia from NH_4Cl , however, a chemical reaction with lime milk is necessary. It takes place according to the following reaction equation:



The addition of lime milk simultaneously leads to the separation of ammonia bound as sulfate:



The carbon dioxide required for the carbonisation and the lime milk required for the NH_3 -recovery are generated by burning the limestone, according the following reactions:



Before being fed into the CO_2 -compressors, which take the off-gas from the furnace and lead it into the carbonisation, the hot and dust-loaded gas is cooled and cleaned in direct exchange with water.

In order to obtain a highly concentrated CO_2 -gas, the excess of air and the consumption of coke should be as small as possible, even if a part of the CaCO_3 remains unburned. Besides coke, also natural gas is used as fuel. The caustic lime leaving the furnace is changed in horizontal trick drums under the addition of used cooling water to a most concentrated suspension of lime milk. The lime milk is then used for the distillative recovery of the ammonia as well as for the brine cleaning. In the case of the manufacturing plant of Matthes & Weber, one of the plants used as data source in UBA (2001), lime milk is not generated for the ammonia recovery, but CaO is led directly to the NH_3 -distillation (dry lime process).

The limestone volume depends on the quantity of caustic lime required for the ammonia recovery. On this occasion an excess of carbonic acid is generated, that is either discharged into the atmosphere or handed over to other consumers.

The residual lye of the ammonia recovery (final lye) mainly contains calcium chloride besides sodium chloride and unconverted lime components and is discharged as waste water.

Quality specifications of the final product soda

According to Thieme (1993), the soda obtained by the ammonia-process described above is, after calcination, an anhydrous, technical-grade soda. A typical analysis is given:

Na_2CO_3 : 99.6%	NaCl : 0.15%	Na_2SO_4 : 0.2%
Fe_2O_3 : 0.002%	CaO : 0.01%	MgO : 0.02%

In addition to its chemical analysis, the product is also characterized by particle size and bulk density.

Heavy ash production

As described above, for the most part "heavy ash" is manufactured from light ash by the so-called "monohydrate route". To produce heavy ash, with particle size and bulk density to match those of the glassmakers's sand, light ash is first reacted with water to give soda monohydrate crystals. These are then dehydrated by heating in a calciner either similar in design to the light ash calciner or in a steam-heated fluid-bed calciner. Heavy ash is also manufactured by a process which does not involve the crystallization of soda monohydrate. Light ash is compacted directly using mechanical pressure; the compacted material is broken to suitable size, graded and dedusted for sale. Although superficially this method may appear to be more economic and less energy intensive, this is not necessarily so because of equipment cost and consumption of electricity. Besides, the product quality is not identical with that

produced by the monohydrate route. Nevertheless, for this study the production of heavy ash is not considered.

Soda by-products generated in the Solvay process

When producing soda by means of the Solvay technique, the following by-products can be generated:

- Calcium chloride (CaCl_2)
- Refined sodium bicarbonate (NaHCO_3)
- Sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$)
- Washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)
- Ammonium chloride (NH_4Cl)
- Precipitated calcium carbonate (CaCO_3)

The relationship between soda ash production and the production of the by-products mentioned above is summarised in Fig. 72.2. Concerning these different by-products, the only one taken into account in this study here is calcium chloride due to the fact that this is the main production way here in Europe. Thus, an allocation has to be made – for more details see chapter 72.5.7.

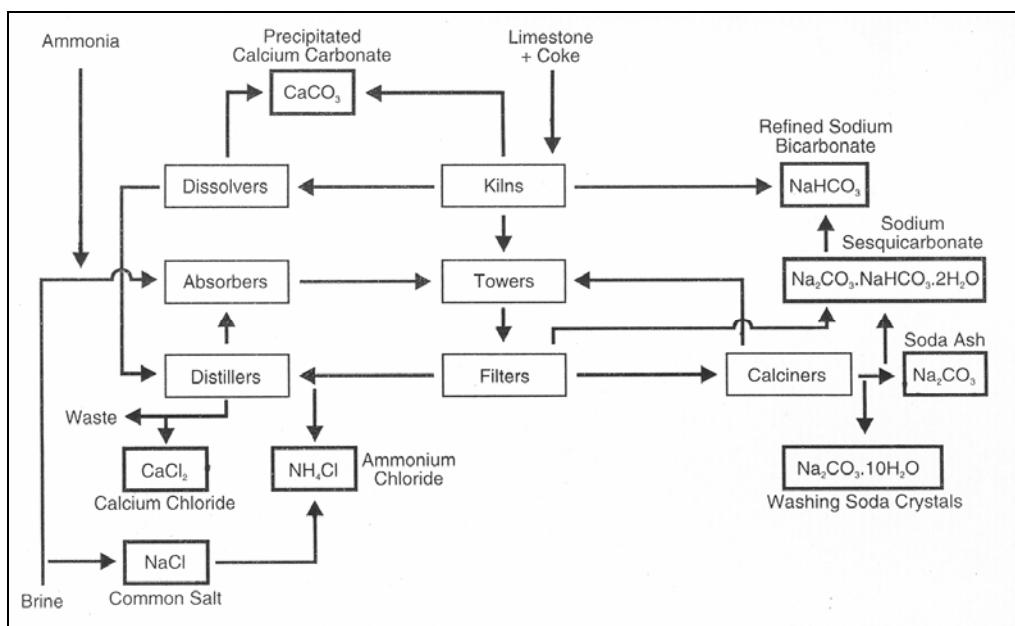


Fig. 72.2 Soda by-products generated by means of the Solvay technique (taken from Fig.11, Woode (1995))

72.4 System Characterisation

This report corresponds to the module in the Ecoinvent database for the **production of soda and calcium chloride** by means of the **Solvay process**. The respective functional unit of the allocated co-products are **1 kg soda, powder, at plant, in Europe** resp. **1 kg calcium chloride, CaCl₂, at plant, in Europe**.

For this study the production of soda ash by means of **Solvay process** is considered, since this is the one currently in use in the European industry. The production of heavy ash starting from light soda ash is not considered, since there is no enough information available regarding this process. According to UBA (2001) the typical manufacturing plant considered for this study will be the plant shown in Fig. 72.1. **All data are referred to 1 kg 100% soda.**

The average production capacity from three German manufacturing plants cited in UBA (2001) is 500 tones per year. For this study this is assumed to be a typical production capacity for the European industry. The system includes the process with consumption of raw materials, auxiliaries, energy, infrastructure and land use as well as the transportation of the raw materials, auxiliaries and wastes. Generation of wastes and emissions to air and water are also considered. The system does not include transportation or storage of the final product soda.

Transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers. Wastes are assumed to be sent to landfill.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

72.5 Soda production, solvay-process, at plant (RER)

72.5.1 Data sources

The main data source for this study is UBA (2001), a German report on the best available techniques (BAT) for soda production. This source presents data from 1999 from two German manufacturing plants: Solvay Soda Deutschland, located in Rheinberg and a production plant from the company Matthes and Weber, in Duisburg. The latter gave up the production at the end of the year 1999, but for the purpose of this study their data are also considered.

Additional information is taken from Thieme (1993), KCL (2002) and Woode (1995). In this latter, each chapter is written by an industrial expert. The disadvantage of this source is that it does not mention the origin of the values reported.

Thieme (1993) is written by a technical expert from the soda industry. Data from this source regarding consumption of raw materials are analysed. It does not mention the origin of the values reported.

KCL (2002) is a Finnish lyfecycle inventories database. KCL is a Finnish pulp and paper research company. The data presented in the study correspond to an average finnish technology level; the date when the data were taken is unknown as well as how the data have been aquired.

When several values are available in the different data sources, an average is taken and the range is indicated in the form of percent variability ($\pm\%$).

72.5.2 Raw materials and auxiliaries

The principal raw materials required for the manufacture of soda are sodium chloride, limestone (calcium carbonate), ammonia, water and air. Natural gas and coke used as fuel are considered in the energy chapter below. The quantity of limestone used per kg of soda ash produced is determined solely by the amount of calcium oxide required for ammonia recovery. According to Thieme (1993), the consumtion of 95% pure limestone varies between 1.1 to 1.2 kg per kg soda produced and is therefore 10 to 20 % higher than the theoretical value.

Regarding the purity of the raw materials used, brine always contains impurities that have to be removed in the process. Thieme (1993) indicates that limestone must be of high purity, i.e. with a SiO₂-content of less than 3% and also a Fe₂O₃-Al₂O₃-content of less than 1.5%.

In regard to water, UBA (2001) indicates a consumption of approximately 0.08 m³. kg⁻¹ 100% NaCO₃.

Tab. 72.3 gives an overview of the information about consumption of raw materials and auxiliaries in the different sources used.

Tab. 72.3 Consumption of raw materials and auxiliaries in the Solvay process in the different sources used

(kg.kg ⁻¹ 100% NaCO ₃)	UBA 2001	Thieme 1993	KCL 2002	This study
NaCl		1.50 E+00	1.50 E+00	1.50 E+00
CaCO ₃	1.20 E+00	1.15 E+00	1.20 E+00	1.20 E+00
NH ₃			4.00 E-01	

For ammonia, the number in KCL 2002 seems too high if considering the recovery actually in use in the industry. Therefore, this value is not taken into consideration. Instead, the value for loss of ammonia as emission into air during the process is taken, considering that this is the amount that has to be replaced. This value is 2.00 E-03 kg NH₃ per kg soda manufactured.

72.5.3 Energy and transportation

Energy

According to Woode (1995), the ammonia-process is a substantial user of energy in the form of heat. Much of the heat is required at relatively low temperatures, 100 to 200 °C, and so can be supplied as low- and intermediate-pressure steam, after first using the high pressure to generate electricity in turbo-alternators. Heat can also be recovered from various process streams, so fresh boiler feed water can be pre-heated this way prior to feeding to the boilers.

Concerning the consumption of energy in the soda production, Tab. 72.4 gives an overview of the information available in the sources used.

Tab. 72.4 Consumption of energy in the Solvay process in the different sources used.

(kg ⁻¹ 100% Na ₂ CO ₃)	UBA (2001)	KCL (2002)	This study
electricity	kWh	4.00 E-02	4.00 E-02
hard coal	kg	3.00 E-01 kg (\pm 70%)	2.50 E-01

When a value is an average of data from the source, the range is indicated in ±%.

UBA (2001) mentions the consumption of electricity but does not present any value. Therefore, both values for electricity and hard coal are taken from KCL (2002).

Transportation

Concerning transportation of raw materials and auxiliaries, no precise information about distances is available in the examined data sources. Accordingly to Woode (2001) it is assumed that the majority of the plants are close to their respective sodium chloride and calcium carbonate suppliers. The first is in some cases also delivered to the near manufacturing plants just by pipeline. Due to a lack of further information, 20 km by lorry are assumed for NaCl and 100 km by lorry for CaCO₃.

For wastes produced within the process, standard distances as defined in Firschknecht et al. (2004b) are used. Thus, and assuming also that the wastes are sent to landfill, 10 km on the road by lorry are considered. A 32 tonnes lorry is assumed in order to facilitate the calculations of the total transport amounts for the database. Tab. 72.5 summarises the total transport amounts and means for the production of 1 kg of soda.

Tab. 72.5 Total transport amounts and means for the Solvay process.

(tkm. kg ⁻¹ 100% Na ₂ CO ₃)	lorry	train
raw material (NaCl)	3.00 E-02	0
Auxiliaries (CaCO ₃)	1.20 E-01	0
waste to disposal sites	2.50 E-03	0
Total transports	1.53 E-01	0

72.5.4 Infrastructure and land-use

There is no information available about infrastructure and land-use of Solvay-process plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. This estimated value is 4.E-10 unit. kg⁻¹ chemical.

72.5.5 Emissions to air and water

Data from UBA (2001) are used in this study. The values presented in the mentioned source are based on the emission declaration of Solvay for the year 1996 according German Immission Directive. These values are taken from different measurements and systems. Basis of the data are average half-hour-measurements of external analyses institutes, average concentrations from on-line measurements as well as internal company measurements and calculations. UBA (2001) presents data about essential emission sources as well as the concentrations emitted into the atmosphere. For this study, only ammonia emissions to air are taken into account – all other emissions are from the combustion of coal and thus already included in the used coal dataset. Another data source for emissions is KCL (2002).

Regarding **emissions to water**, UBA (2001) mentions the following three waste water sources:

- waste water from the brine cleaning
- wash water from the off-gas treatment (lime oven)
- final lye from the NH₃ distillation

In the both manufacturing plants analysed by UBA (2001) these effluents are discharged together into the recipient. While the solid materials from the brine cleaning are mainly composed by precipitation products, the solid materials of the final lye are essentially caused by pollutants in the used lime and the coke used for the burning. The effluent goes to a sedimentation basin were most of the solids are settled prior discharge. After the sedimentation step the effluent has a load of max 2.00 E-03 kg solids.kg⁻¹ soda.

UBA (2001) presents values for volume of waste water and emissions into water, corresponding to the manufacturing plants from Solvay Rheinberg and Matthes & Weber - Duisburg. These data are measuring results of the official examinations for the year 1999. In the case of Solvay Rheinberg 21 measurements were done, in the case of M. & W., 8 measurements. Basis of these measurements is the

qualified spot check. Minimum and maximum values are reported. For this study an average from the mentioned data is reported, as well as the range of values.

Tab. 72.6 Emissions to air (only process emissions) and emissions to water of the Solvay process in the different sources used.

(kg ⁻¹ 100% Na ₂ CO ₃)	UBA (2001) ¹	KCL (2002)	Woode (1995)	This study
<i>Emission to air</i>				
NH ₃ kg	5.80 E-05	2.00 E-03		2.00 E-03
<i>Emission to water</i>				
Wastewater m ³	7.85 E-03 (± 11%)		1.00 E-02	1.00 E-02
Total Nitrogen kg	1.85 E-04			1.85 E-04
P kg	5.21 E-05 (± 50%)			5.21 E-05
Ca kg	3.39 E-01 (± 3%)			3.39 E-01
Cd kg	1.73 E-07 (± 80%)			1.73 E-07
Clorides kg	9.00 E-01 (± 30%)			9.00 E-01
Cu kg	1.65 E-06 (± 45%)			1.65 E-06
Hg kg	1.75 E-09(± 100%)			1.75 E-09
Ni kg	1.15 E-06 (± 60%)			1.15 E-06
Pb kg	1.49 E-05 (± 200%)			1.49 E-05
solid substances, unspecified kg	9.93 E-02 (± 50%)			9.93 E-02

When a value is an average of data from the source, the range is indicated in ±%.

¹ Average from measuring data from Solvay Rheinberg and Matthes & Weber –Duisburg corresponding to official examinations for the year 1999. For NO₂-N data correspond solely to Solvay Rheinberg.

² Based on emission values calculated for burning of hard coal. See Table 1.5 above.

³ Reported as "residues" in the literature source.

The ammonia value reported by UBA (2001) is up two magnitude order lower than the corresponding values from KCL (2002). Thus, for this study here the value from KCL has been used.

For all emissions into water, the only available values are taken (UBA (2001)), except for wastewater volume. Again, the highest value is used (Woode (1995)).

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. Basing on this assumption and doing the necessary conversion from kWh to MJ is done according to Frischknecht et al. (2004b). Thus, considering the energy input of 4.00 E-02 kWh. kg⁻¹ 100% NaCO₃, the value of waste-heat taken for this study is 1.44 E-01 MJ.kg⁻¹ 100% NaCO₃.

72.5.6 Solid wastes

In regard to solid wastes, UBA (2001) mentions that the separation of the solids from the industrial waste water causes sludge, heavily loaded with chlorides, which is deposited in sedimentation basins. There is no further information about the amount of this waste or about its final disposition.

According to Woode (1995), the manufacturing of soda by means of the ammonia-soda process produces an average of 0.25 kg (0.1 to 0.4 kg) solid waste per kg of soda manufactured. The main sources of the insoluble solids for disposal are the impurities in the limestone and salt (brine) and fuel used. Therefore, and due to lack of further information about the composition of the wastes mentioned, the module considered most appropriate to report solid waste in ecoinvent database is “disposal, inert waste, 5% water, to inert material landfill.”

72.5.7 Allocation factors

As already mentioned, the Solvay process is considered in this study as a multioutput process, resulting in two different products (soda and calcium chloride) and thus, an allocation has to be established for the above described environmental loads (inputs, outputs).

Based on the world market prices of the two products, a simple allocation according to the price is established here, resulting in allocation factors of 0.67 for calcium chloride and 0.33 for soda. Although both products have their specific finalization steps (purification etc.), this allocation factor is used for all inputs and outputs due to a lack of more specific information.

72.5.8 Data Quality Considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

All data regarding emissions to water are from UBA (2001). This is a qualified source but it has disadvantage that the information summarised corresponds just to two modern manufacturing plants. Data regarding emissions to air are taken from KCL (2002). KCL (2002) has the disadvantage that there is no information about the origin of the data. The module analysed corresponds to Europe. However, the data used for this study correspond to Germany in one case and Finland in the other. This lack of representativeness is reflected in the uncertainty scores.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a lack of data, assumptions based on Frischknecht et al.(2004b) (transport) resp. the very general module of an organic chemical plant are used.

Tab. 72.7 summarizes the input and output data as well as the uncertainties used for the production of soda and calcium chloride. The values are given for the production of 1 kg 100% soda. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 72.9.

Tab. 72.7 Input- / Output-data for the soda production by means of the Solvay process (expressed per kg 100% soda produced)

Explanation	Name	Location	Unit	soda production, solvay process, at plant			GeneralComment	soda, powder, at plant	calcium chloride, CaCl ₂ , at plant
				RER	0	kg			
				Uncertainty	StandardDeviation95%	Type			
Resources Input from Technosphere	Water, unspecified natural origin		m ³	8.00E-2	1	1.09	(1.3,1.3,1.3); data from survey in literature (UBA 2001)	33	67
	sodium chloride, powder, at plant	RER	kg	1.50E+0	1	1.63	(4.3,5,3,1.5); data from survey in literature (Thieme 1993 and KCL 2002)	33	67
	limestone, milled, packed, at plant	CH	kg	1.20E+0	1	1.22	(1.3,1,3,1.5); data from survey in literature (UBA 2001 and KCL 2002)	33	67
	ammonia, liquid, at regional storehouse	RER	kg	2.00E-3	1	1.57	(3.3,5,3,1.5); calculated values for loss during the process. numbers for loss taken from data from survey in literature (KCL 2002)	33	67
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	4.00E-2	1	1.58	(3.3,5,3,1.5); data from survey in literature (KCL 2002)	33	67
	heat, at hard coal industrial furnace 1-10MW	RER	MJ	7.23E+0	1	1.58	(3.3,5,3,1.5); data from survey in literature (KCL 2002)	33	67
	transport, lorry 32t	RER	tkm	1.53E-1	1	2.05	(4,na,na,na,na); Standard distances and estimation	33	67
	chemical plant, organics disposal, inert waste, 5% water, to inert material landfill	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); Estimation	33	67
		CH	kg	2.50E-1	1	1.68	(4,5,5,1,1.5); data from survey in literature (Wooode 1995)	33	67
								100	0
Output air emission water emission	soda, powder, at plant	RER	kg	1.00E+0				0	100
	calcium chloride, CaCl ₂ , at plant	RER	kg	1.05E+0					
	Heat, waste		MJ	1.44E-1	1	1.58	(3.3,5,3,1.5); calculated from electricity input	33	67
	Ammonia		kg	2.00E-3	1	1.84	(3.3,5,3,1.5); data from survey in literature (KCL 2002)	33	67
	Nitrogen		kg	1.85E-4	1	1.51	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67
	Phosphorus		kg	5.21E-5	1	1.51	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67
	Calcium, ion		kg	3.39E-1	1	1.51	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67
	Cadmium, ion		kg	1.73E-7	1	5.01	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67
	Chloride		kg	9.00E-1	1	1.51	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67
	Copper, ion		kg	1.65E-6	1	1.51	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67
	Mercury		kg	1.75E-9	1	5.01	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67
	Nickel, ion		kg	1.15E-6	1	5.01	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67
	Lead		kg	1.49E-5	1	5.01	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67
	Solids, inorganic		kg	9.93E-2	1	1.51	(1.3,1,3,1.3); data from survey in literature (UBA 2001)	33	67

72.6 Calcium chloride, CaCl₂, at regional storage

72.6.1 System Characterization

The dataset of calcium chloride at regional storage was assessed according to Fig. 72.3.

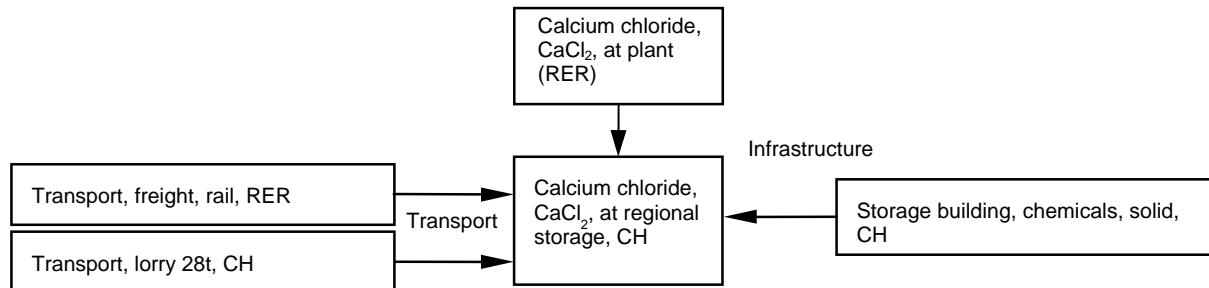


Fig. 72.3 Process chain for the regional storage process of calcium chloride

72.6.2 Process

It was assumed that transport to Switzerland occurs with bulk rail cars (30-90 t) and bulk trucks (20 t). The transportation distances were assumed to be similar to the standard distances for soda ash (Na₂CO₃) of 600 km rail transport and 50 km road transport. For the rail transport a process with European location (RER) was used due to the fact that the larger part of the distances occur outside Switzerland. For the road a process for Switzerland was applied (28 t lorry) with the assumption that this transport includes mainly the delivery to the customer which occurs in Switzerland. Because the inventory refers to the weight of active materials the calculated transport demand has to be multiplied by 1.3 (for 77% CaCl₂ in the product). This leads to an amount of 0.78 tkm rail transport and 0.065 tkm road transport per kg CaCl₂.

Further the infrastructure of the storage building was included. The used process for bulk chemical storage refers to sodium chloride storage which was assumed to be similar. According to the data in the process “” this infrastructure refers to an annual throughput of 0.23 Mt. Assuming an life time of

the building of 50 years, $87 * 10^{12}$ units of the infrastructure have to be accounted per kg material. Because the inventory refers to the weight of active materials this amount has to be multiplied by 1.3 (for 77% CaCl₂ in the product).

The assessed process includes only the transport to Switzerland, the building construction and disposal and the land use for the building and the surrounding service area. Further it was assumed that the bulk storage area is not heated and therefore no burden for the production of room heat was included. There were no burdens included for package materials and further energy or infrastructure needed for the overhead of a local reseller.

72.6.3 Data quality considerations

Tab. 72.8 shows the data quality indicators for the inventory of the process for regional storage of calcium chloride in Switzerland. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. The highest uncertainties exist for the infrastructure data because of missing specific data an approximation with an similar chemical product (NaCl) was used. For the transport distances standard values were used and therefore the representativity is not known. Further uncertainty will arise due to neglected impacts as package materials, the possible room heating of a part of the building and expenditure for the overhead of a local company (e.g. reseller). Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 72.9.

Tab. 72.8 In- / Outputs for the module “calcium chloride, CaCl₂, at regional storage”, location CH

Explanation	Name	Location	Unit	calcium chloride, CaCl ₂ , at regional storage		GeneralComment
				CH	0	
				kg	kg	
Input from Technosphere	calcium chloride, CaCl ₂ , at plant storage building, chemicals, solid	RER	kg	1.00E+00	1	exact value
	transport, lorry 28t	CH	unit	1.13E-10	1	(4,5,1,1,3,5); Approximation from data of NaCl production
	transport, freight, rail	CH	tkm	6.50E-02	1	(4,5,nA,nA,nA,nA); Estimated with standard distances for soda ash
	calcium chloride, CaCl ₂ , at regional storage	RER	tkm	7.80E-01	1	(4,5,nA,nA,nA,nA); Estimated with standard distances for soda ash
Output	calcium chloride, CaCl ₂ , at regional storage	CH	kg	1		

72.7 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

72.8 Conclusions

Average European datasets for the production of soda and calcium chloride by the Solvay process for the year 2000 are established.

All these datasets are in accordance with the present quality guidelines of the ecoinvent project and are based on reports covering the European industry. The main part is from a german study – reporting measured data for the year 1999. The data are thus of a good quality and can be used in a very broad context.

72.9 EcoSpold Meta Information

ReferenceFunction	Name	soda production, solvay process, at plant	calcium chloride, CaCl2, at regional storage
Geography	Location	RER	CH
ReferenceFunction	InfrastructureProcess	0	0
ReferenceFunction	Unit	kg	kg
ReferenceFunction	IncludedProcesses	<p>Manufacturing process by means of the Solvay technique is considered, including the consumption of raw materials, auxiliaries, energy, infrastructure and land use, as well as transport of the raw materials, auxiliaries and wastes. The system also includes the generation of wastes and emissions into air and water. Transport and storage of the final product soda are not included. No byproducts or coproducts are considered. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to landfill. Most data are from a German study based on measurements in two German plants. A Finnish study bases also on data from one plant, but no background information about the data is available. The other sources are literature data and estimations. Highest value is taken (conservative criterion). Inventory refers to 1 kg 100% soda, powder, at plant. The p</p>	Transport to Switzerland and storage area included. Transport as bulk material assumed and therefore no package materials or package processes included. This module includes no calcium chloride produced from brine as used in the U.S.
ReferenceFunction	Amount	1	1
ReferenceFunction	LocalName	Natriumcarbonat, Pulver, ab Werk	Calziumchlorid, ab Regionallager
ReferenceFunction	Synonyms	sodium carbonate // soda ash // ash	
ReferenceFunction	GeneralComment	The multioutput process "soda production, Solvay process, at plant" delivers the coproducts "soda, powder, at plant" and "calcium chloride, CaCl2, at plant". An allocation to the two products is done by using the prices, resulting in soda 33% and calcium chloride 67%.	For this inventory it was assumed that the main source of calcium chloride used in Switzerland originates from soda ash plants in europe.
ReferenceFunction	CASNumber		010043-52-4
Time Period	StartDate	1999	1998-01
Time Period	EndDate	1999	2000-12
Time Period	DataValidForEntirePeriod	1	1
Time Period	OtherPeriodText	Most of the data correspond to measurements performed in 1999. The other sources do not mention the time when the data were obtained and may be updated.	
Geography	Text	Data are from measures at European manufacturing plants or estimations considering the European situation	No production of calcium chloride in Switzerland. Import from Europe assumed.
Technology	Text	Data from Finnish and German literature source refer apparently to state-of-the-art manufacturing plants.	Only calcium chloride from soda ash production considered. Standard transport distances for soda ash used. Infrastructure based on sodium chloride storage.
Representativeness	Percent		
Representativeness	ProductionVolume	unknown	unknown
Representativeness	SamplingProcedure	see geography and technology	No validated information available on representativeness of used processes.
Representativeness	Extrapolations	Transports based on standard distances of Ecoinvent. Infrastructure: proxy module used (chemical plant, organics)	Assumed that 100% of the total calcium chloride consumption in Switzerland originates from the soda ash process.
Representativeness	UncertaintyAdjustments	none	none

72.10 References

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73 Sodium chlorate

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 Review: Heiko Kunst, TU Berlin

73.1 Introduction

Sodium chlorate (NaClO_3 , CAS-No. 7775-09-9) is a white, hygroscopic, crystalline solid. It is an efficient oxidising agent. Sodium chlorate is soluble in water. The most important chemical and physical properties are summarised in **Tab. 73.1**.

Synonyms for sodium chlorate: chlorate of soda, sodium salt of chloric acid.

Tab. 73.1 Chemical and physical properties of sodium chlorate (Chemfinder 2002).

Property	Value	Unit	Property	Value	Unit
Molecular weight	106.441	g mol^{-1}	Melting point	248	°C
Density (at 20°C)	2.49	g cm^{-3}	Boiling point	300	°C

The following description of production technology and the use of nitric acid are summarised from Winzer (1986) and Eka (2000).

73.2 Reserves and Resources

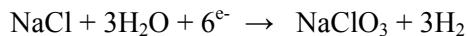
Sodium chlorate is produced basically from sodium chloride. Therefore, the resources available as well as the reserves are the same as for the production of sodium chloride, described in Chapter 74.

73.3 Production Technologies and Use

73.3.1 Production technologies for sodium chlorate

Process basis

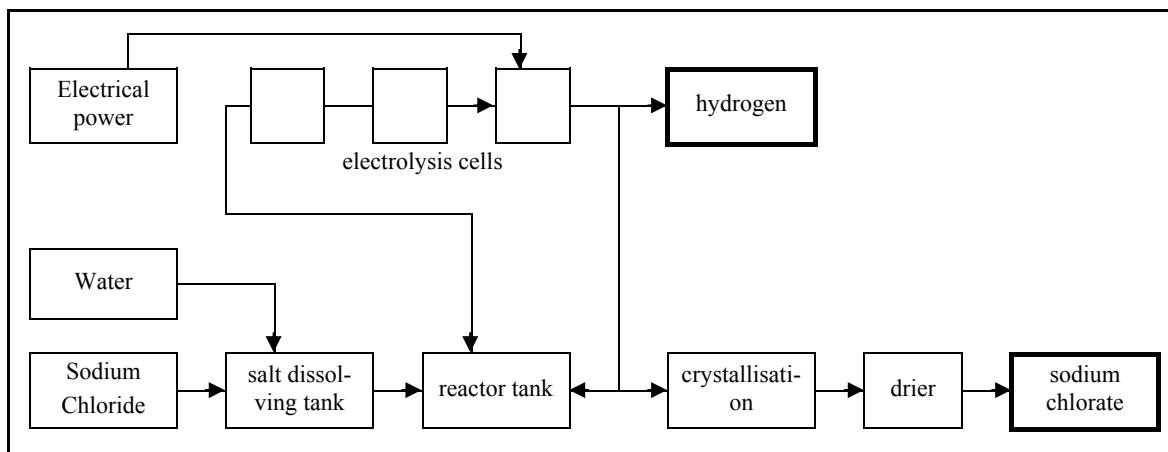
Sodium chlorate is produced by electrolysis of an aqueous sodium chloride solution. (See following figure) This is achieved according the following overall reaction equation:



The concentrated chlorate solution is either submitted to crystallisation or it is used directly, particularly in the production of chlorine dioxide.

Sodium chlorate, hydrogen gas (H_2) and heat are formed in the production process. The solution formed is crystallised and the chlorate crystals are separated, washed and dried. The final product contains mostly 99 to 99.9% sodium chlorate. The hydrogen gas and the heat produced can be exported for different uses.

The main raw materials are sodium chloride and water. Energy is provided by electrical power.

Fig. 73.1 Simplified schema of sodium chlorate production. (Taken from Fig. 1 in Eka (2000))

An aqueous solution of sodium chloride is electrolysed, usually in cells without a diaphragm. Hydrogen and sodium hydroxide are formed at the cathode, while chloride is discharged at the anode. Chlorine does not evolve as a gas, but undergoes hydrolysis:



Chlorate then forms simultaneously by two competing reactions: (1) predominantly by autooxidation of hypochlorite in the bulk electrolyte, and (2) to a small extent (ca. 20%) by anodic chlorate formation.

Some electrosynthesis systems combine the cell and the chemical reactor in a single unit. Other industrial systems are composed of an electrochemical reactor and a separate chemical reactor interconnected by electrolyte circulation pipes with integrated heat exchangers for the removal of excess heat or separate heat exchangers. None of these electrosynthesis systems is clearly superior from an engineering point of view.

Regarding the types of electrolysis cell currently in use, most (90 to 95%) of the cells are equipped with coated titanium anodes.

Modern electrochemical reactors cover the complete spectrum of unipolar and bipolar electrodes, including direct coupling of cells with unipolar electrodes, an arrangement sometimes called multipolar. Cells with unipolar electrodes are suitable for large currents up to 100kA, while cells with bipolar electrodes seldom exceed 30 kA. Multipolar cells combine some of the advantages of cells with unipolar and bipolar electrodes.

Auxiliary processes before/after electrolysis cell

Brine purification:

The brine must not contain large amounts magnesium and calcium, which could form deposits on the cathodes. Sodium carbonate and sodium hydroxide are added to the brine to raise its pH to at least 10. The sulphate concentration must be lower 10-20 g/L. The brine must be free of heavy metals that favour the decomposition of hypochlorite.

Crystallisation:

For the crystallisation of chlorate, a solution of sodium chloride is produced. The temperature at the cell outlets is first raised to convert the remaining of hypochlorite into chlorate. Urea, ammonia, hydrogen peroxide or sodium formate is added to complete the hypochlorite decomposition. The solution is then rendered slightly alkaline with NaOH (this reduces corrosion in the crystalliser). The NaClO₃ solution is subsequently fed to a vacuum crystalliser based on flash cooling with subsequent crystalli-

sation. Christalline chlorate is separated from sodium chloride solution by cooling or evaporation. Moist chlorate crystals are dried in a fluidised bed type dryer. Drying air is heated with either electrical power or steam. The dryer and the transportation equipment are connected to a scrubber for chlorate dust removal. Dry chlorate is normally stored in silos before being loaded into trucks, rail cars or big bags.

The hydrogen gas leaving the cellboxes contains some oxygen and chlorine. The gas mixture is thus washed with caustic soda solution in absorption towers for removal of chlorine before it can be used for burning or released to the atmosphere. When the hydrogen will be used as raw material for other purposes, it might be necessary also to eliminate the oxygen content. This can be easily accomplished by passing the gas through a catalytic bed where any remaining oxygen reacts with hydrogen to form water.

The purity requirements of the final product sodium chlorate depend on the intended purpose and are usually negotiated between producer and user. Mostly, a purity of 99 to 99.9 % is required.

73.3.2 Use

Sodium chlorate is used in the manufacture of chlorine dioxide bleach for the pulp and paper industry. The once predominant use of sodium chlorate as a non-selective herbicide has strongly declined. Second in importance is its use as an intermediate in the production of other chlorates, mainly potassium chlorate, and of sodium perchlorate for conversion to ammonium perchlorate, which is used as an oxidiser in solid propellants. Sodium chlorate is further used as oxidising agent in uranium refining and other metallurgical operations, as an additive to agricultural products and dyes, in textile and fur dyeing, metal etching, and in chemical laboratories and throughout the chemical industry as an oxidising agent.

73.4 System Characterisation

This report corresponds to the module in the ecoinvent database for the **production of 1 kg sodium chlorate, powder, at plant, in Europe**.

As mentioned before, the production with the electrolysis cell process is considered, taken into account different process modalities that are currently in use. **All data in this study are referred to 1 kg sodium chlorate 100%.**

Regarding to the production capacity in the manufacturing plants, 160 t.d^{-1} 100% NaClO_3 is an average value from the European plants analysed in Fawer 2002, being the range of production capacity from these plants 20 to 200 t.d^{-1} 100% NaClO_3 . For this study this average (160 t.d^{-1}) is the value adopted since it corresponds to the source from which most data are taken.

If taking the values presented in Winzer (1986) for the five European plants, the average capacity is 990 kg.d^{-1} 100% NaClO_3 , being the capacities in the mentioned plants within a range from 560 to 1370 kg.d^{-1} . These production capacities are much below the mentioned in Fawer 2002.

Regarding H_2 , the average production according Fawer (2002) is 8.9 t.d^{-1} H_2 . Nevertheless no information is given about the amount vented or destined for reuse or exported. If taking the data in Winzer (1986), an average production capacity is approximately 59 kg. d^{-1} , within a range from 27 to 80 kg.d^{-1} , depending on the manufacturing plant.

The system includes the consumption of raw materials, auxiliaries, energy and infrastructure and land use, as well as the generation of solid wastes and emissions to air and water. It also includes the transportation of the raw materials, auxiliaries and wastes. It does not include transportation of the final product nitric acid. Hydrogen gas could be considered as the by-product generated in the production process. Nevertheless, according the information available, depending on the company, variable a-

mounts of hydrogen are vented to the atmosphere and neither used in the same plant nor exported. Therefore, for this study, hydrogen is considered an emission into air.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage is also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to landfill.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

73.5 Sodium Chlorate Production Process

73.5.1 Data sources

Main data source for this study is Fawer (2002)³. Winzer (1986) has been taken into account for plausibility checks and comparison reasons.

Fawer (2002) is a personal communication on the background information for Bowsted and Fawer (1996), regarding confidential data of European manufacturing plants. This information allows disclosing the data from Bowsted and Fawer (1996) in a suitable manner for the present study. For this study averages of values corresponding to six companies are presented.

Bowsted and Fawer (1996) is an Ecoprofile on sodium chlorate developed under an initiative of the Sodium Chlorate Group at the European Chemical Industry Council (CEFIC). The study bases on confidential data from 1994 provided by the industry, previous works carried out by CEFIC, as well as other reports. In this source not only the manufacturing process itself is considered, but all the process from the extraction of the raw materials and the energy production. Therefore a disclosure of this information is necessary if used for ecoinvent database.

Winzer (1986) presents data from eight manufacturing companies regarding different operational parameters, energy and raw materials consumption as well as production rates. For this study the data corresponding to the five European companies from the eight companies mentioned are used. This source does not provide with values concerning emissions and wastes. One disadvantage of this source is that the information summarised may be quite outdated.

When several values are available in the different data sources, an average is taken and the range is indicated in the form of percent variability ($\pm\%$).

73.5.2 Raw materials and auxiliaries

The main raw material for the production of nitric acid is NaCl, and the most relevant auxiliaries are HCl, NaOH and Na₂Cr₂O₇.

Tab. 73.2 gives an overview of the information about the consumption of raw materials and auxiliaries in the different sources used. The main use of these materials is also indicated.

Regarding water, Tab. 73.3 shows the average water consumption based on the six plants mentioned in Fawer (2002). The principal uses of the water are also indicated. As can be seen in the table, there is a very high variability among the different plants regarding water consumption.

³ Fawer M. (2002). Personal communication on July 2002.

Tab. 73.2 Consumption of raw materials and auxiliaries for the production of sodium chlorate.

Input (kg.kg ⁻¹ 100% NaClO ₃)	Main purpose in the process	Winzer 1986 ¹	Fawer 2002	This study
NaCl	salt solution for electrolysis	5.60 E-01 (± 2%)	5.66 E-01 ² (± 4%)	5.66 E-01
HCl (100%)	maintain optimal pH-value for electrolysis	1.21 E-02 (± 30%)	1.74 E-02 ³ (± 50%)	1.74 E-02
NaOH (100%)	- brine purification - control of pH - washing H ₂ cellgas scrubber	9.3 E-03 (± 90%)	2.05 E-02 ⁴ (± 40%)	2.05 E-02
Na ₂ Cr ₂ O ₇ (100%)	- suppression of corrosion of Fe-cathodes - inhibition of anodic oxygen formation - suppression of cathodic ClO ⁻ and ClO ₃ ⁻ reduction - buffering of electrolyte in optimal range	3.40 E-04 (± 80%)	4.20 E-04 ³ (± 70%)	4.20 E-04
Na ₂ SO ₃			4.07 E-05 ⁵	4.07 E-05
Na ₂ CO ₃	removal of Ca, Mg, Fe and sulphates from the brine		4.38 E-04 ⁶ (± 60%)	4.38 E-04
CaCl	removal of Ca, Mg, Fe and sulphates from the brine		1.73 E-04 ⁵	1.73 E-04
H ₂ O ₂ (100%)	removal of NaOCl in electrolysis effluent		1.91 E-03 ⁶ (±5%)	1.91 E-03

When a value is an average of data from the source, the range is indicated in ±%.

¹: all values are average from 4 European manufacturing plants

²: average from 5 European manufacturing plants

³: average from 4 European manufacturing plants

⁴: average from 6 European manufacturing plants

⁵: value corresponding to one European manufacturing plant

⁶: average from 2 European manufacturing plants

In order to harmonise the database and link the sodium chlorate inventory with the hydrochloric acid inventory, in this study, hydrochloric acid is reported as „hydrochloric acid 30% in water“. The same for „hydrochloric acid 30% in water“ and „hydrogen peroxide 50% in water“, since these are the names of the corresponding modules in ecoinvent database. Nevertheless, the values reported correspond to 100% of the active substances.

Tab. 73.3 Water consumption for the production of sodium chlorate. Values extracted from Fawer (2002).

$\text{m}^3 \cdot \text{kg}^{-1}$ 100% NaClO_3	
cooling water ¹	1.41 E-01 ($\pm 100\%$)
process water ²	4.32 E-03 ($\pm 80\%$)
washing water ³	1.63 E-04 ($\pm 100\%$)
TOTAL WATER	1.45 E-01 ($\pm 80\%$)

The values presented are averages of values from the source. The range of the original values is indicated in $\pm\%$.

¹: used for electrolysis and other processes

²: used for NaCl dissolving, etc

³: used for H_2 crystallisation

Both sources report very similar values of raw materials consumption, excepting for NaOH. Since this substance is used for brine purification and pH control the difference between the sources can be due to different operational conditions in the manufacturing plants analysed. For this study, the highest values are used following a conservative criterion.

73.5.3 Energy and transportation

Concerning the energy demand and production of the sodium chlorate production, Tab. 73.4 gives an overview of the reported energy consumption in the different sources available.

Tab. 73.4 Energy consumption for the production of sodium chlorate.

Input . kg^{-1} 100% NaClO_3	Winzer 1986	Fawer 2002	This study
electricity kWh	4.88 ($\pm 7\%$)	5.50 ($\pm 6\%$)	5.50

When a value is an average of data from the source, the range is indicated in $\pm\%$.

Regarding energy consumption there are no significative differences between the two data sources. For this study, the values reported by Fawer (2002) are used, according a conservative criterion.

Concerning transportation of raw materials and auxiliaries, no information about distances is available in the examined data sources. Therefore, for all raw materials and auxiliaries, standard distances as defined in Frischknecht *et al*, (2003) were used (100 km by lorry 32t and 600 km by train). For the transportation of the different wastes produced within the process, again, a standard distance to landfill (10 km by lorry) is taken from the mentioned source. Additionally, it is assumed that the lorry has a capacity of 32 tonnes in order to facilitate the calculations of the total transport amounts for the database.

It is assumed that hydrochloric acid, sodium hydroxide and hydrogen peroxide are delivered as solutions in water (30%, 50% and 50% respectively). This is taken into account for the calculation of the transport amounts. The numbers used for this purpose are: 5.80 E-02 kg hydrochloric acid 30% in water, 4.10 E-02 kg sodium hydroxide 50% in water and 3.82 E-03 kg hydrogen peroxide 50% in water. (All the given values are referred to 1kg 100% sodium chlorate).

Tab. 73.5 summarises the total transport amounts for the production of 1 kg of 100% sodium chlorate.

Tab. 73.5 Total transport distances and means for the production of sodium chlorate.

(tkm. kg ⁻¹ 100% NaClO ₃)	lorry	train
raw material	5.66 E-02	3.40 E-01
auxiliaries	1.04 E-02	6.23 E-02
waste to disposal sites	1.07 E-03	0
Total transports	6.81 E-02	4.02 E-02

73.5.4 Infrastructure and land-use

There is no information available about infrastructure and land-use of sodium chlorate plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. This estimated value is 4.00 E-10 unit. kg⁻¹ chemical.

73.5.5 Hydrogen production

According to Fawer (2002), the sodium chlorate production process generates an average of 5.56 E-02 kg hydrogen.kg⁻¹ sodium chlorate produced. This value is an average of five manufacturing plants. The minimal value reported in this source is 4.94 E-02 and the maximal value is 5.80 E-02 kg hydrogen.kg⁻¹ sodium chlorate.

73.5.6 Emissions to air and water

Fawer (2002) provides with data on several emissions to air and water that result from the manufacturing process. This information is summarised in Tab. 73.6.

According to Winzer (1986), in trouble-free operation, environmental pollution problems do not arise. Wastewater from cleaning tanks and building floors requires appropriate treatment to avoid damage of the water flora by chlorates acting as herbicides. This source does not present any values for emissions.

Tab. 73.6 Emissions to air and water of the production of sodium chlorate. Values taken from Fawer 2002

(kg ⁻¹ 100% NaClO ₃)		
<i>Emission to air</i>		
Cl ₂	kg	2.39 E-06 ¹ (\pm 100%)
NaClO ₃	kg	2.48 E-05 ² (\pm 100%)
<i>Emission to water</i>		
Wastewater	m ³	8.97 E-02 ² (\pm 17%)
Chloride	kg	2.66 E-04 ¹ (\pm 90%)
Chromium6+ (Cr6+)	kg	2.80 E-05 ³ (\pm 100%)
Chlorate (ClO ₄)	kg	1.21 E-03 ⁴
hydrogen chloride (HCl)	kg	6.51 E-05 ⁴
Iron	kg	3.92 E-06 ² (\pm 75%)
other unspecified inorganic substances	kg	2.25 E-02 ⁴

When a value is an average of data from the source, the range is indicated in $\pm\%$.

¹: average from 3 European manufacturing plants

²: average from 2 European manufacturing plants

³: average from 4 European manufacturing plants

⁴: average from one European manufacturing plant

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. Basing on this assumption the necessary conversion from kWh to MJ is done according to Frischknecht *et al.* (2003). Thus, considering the energy input of 5.50 kWh. kg⁻¹ 100% NaClO₃, the value of waste heat taken for this study is 1.98 E+01 MJ.kg⁻¹ 100% NaClO₃.

73.5.7 Solid wastes

In Fawer (2002) solid wastes corresponding to filter residues and sludges are mentioned. Regarding filter residues, 2.42 E-03 kg.kg⁻¹ 100% NaClO₃ is an average from three manufacturing plants, ranging the values from 4.20 E-04 to 5.90 E-03 kg.kg⁻¹ 100% NaClO₃ produced. These residues are sent to landfill. For sludge, only one value is presented, 1.05 E-01 kg.kg⁻¹ 100% NaClO₃, corresponding to one manufacturing plant. According to this source, this sludge comes from the brine purification as well as from the wastewater treatment. It undergoes no special disposal. For this study, solid waste is reported as “disposal, municipal solid waste, 22.9 %water, to sanitary landfill”, due to lack of further information about the composition of the wastes mentioned. This is considered the most appropriate among the different modules available in the database.

73.6 Data Quality Considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

All values are taken from Fawer (2002). Reported data are from few plants; some values regarding emissions correspond to just one plant. As mentioned in section 1.5.1, it is not known how the reported values were obtained. It is also no certainty about the representativeness of this data. The data might be also a little updated. All this leads to higher uncertainty scores.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht *et al.* (2003) (transport) resp. the very general module of an organic chemical plant are used. This lack of representativeness is reflected in the uncertainty scores.

The following table summarises the input and output data as well as the uncertainties used for the production of sodium chlorate. The values are given for the production of 1 kg of 100% sodium chlorate. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 73.9.

Tab. 73.7 Input- / Output-data for the sodium chlorate production (expressed per kg 100% sodium chlorate produced)

Explanation	Name	Location	Unit	sodium chlorate, powder, at plant	RER 0 kg	UncertaintyType	StandardDeviation95%	GeneralComment			
Resources Input from Technosphere	Water, unspecified natural origin		m3	1.45E-1	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	sodium chloride, powder, at plant	RER	kg	5.66E-1	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	hydrochloric acid, 30% in H ₂ O, at plant	RER	kg	1.74E-2	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	2.50E-2	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	sodium dichromate, at plant	RER	kg	4.20E-4	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	sodium sulphate, powder, at plant	RER	kg	4.07E-5	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	soda, powder, at plant	RER	kg	4.38E-4	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	calcium chloride, CaCl ₂ , at plant	RER	kg	1.73E-4	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	hydrogen peroxide, 50% in H ₂ O, at plant	RER	kg	1.91E-3	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	5.50E+0	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	transport, lorry 32t	RER	tkm	6.81E-2	1	2.05	(4,na,na,na,na); Standard distances				
	transport, freight, rail	RER	tkm	4.02E-1	1	2.05	(4,na,na,na,na); Standard distances				
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); Estimation				
	disposal, municipal solid waste, 22.9% water, to sanitary landfill	CH	kg	1.07E-1	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
Waste	sodium chlorate, powder, at plant	RER	kg	1.00E+0							
	Hydrogen		kg	5.56E-2	1	1.34	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	Heat, waste	MJ		1.98E+1	1	1.34	(3.5,3,3,1,5); calculated from electricity input				
	Chlorine		kg	2.39E-6	1	1.65	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	Sodium chlorate		kg	2.48E-5	1	1.65	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	Chloride		kg	3.29E-4	1	1.65	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	Chromium VI		kg	2.80E-5	1	1.65	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	Chlorate		kg	1.21E-3	1	1.65	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	Iron, ion		kg	3.92E-6	1	1.65	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
	Solids, inorganic		kg	2.25E-2	1	1.65	(3.5,3,3,1,5); data from personal communication (Fawer 2002)				
Output air emission											
water emission											

73.7 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

73.8 Conclusions

An average European dataset for the production of sodium chlorate for the year 2000 is established. The dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on a personal communication concerning a report covering the European industry, based on statistics from the middle of the 1990s. The data are thus of a quite good quality and can be used in a broad context.

73.9 EcoSpold Meta Information

ReferenceFunction	Name	sodium chlorate, powder, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Maunfacturing process by means of electrolysis of a sodium chloride solution is considered, starting with this raw material and including brine purification. Final drying of the sodium chlorate crystals is also included, as well as the production of hydrogen gas.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Natriumchlorat, Pulver, ab Werk
ReferenceFunction	Synonyms	chlorate of soda // sodium salt of chloric acid
ReferenceFunction	GeneralComment	Manufacturing process includes raw materials, auxiliaries, energy, transportation, infrastructure and land use, as well as emissions into air and water and wastes. Transport of the raw materials, auxiliaries and wastes is included, transport and storage of the final product are not included. No byproducts or coproducts are considered. Hydrogen is not considered a byproduct from the process, but an air emission. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Solid wastes are considered to be sent to landfill. The values in the report are literature average values, based on Fawer 2002, a personal communication on the background information from Bowstead and Fawer 1996, regarding confidential data of European manufacturing plants. This information allows to disclose the data from Bowsted and Fawer1996 in a suitable manner for the present study. Inventory refers to 1 kg 100% sodium ch
ReferenceFunction	CASNumber	7775-09-9
TimePeriod	StartDate	1990-01
TimePeriod	EndDate	1995-12
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	period correspond to the early nineties, therefore estimated 1990 to 1995
Geography	Text	Average values of six European manufacturing plants
Technology	Text	unknown
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	all data from Fawer 2002, averages from values.
Representativeness	Extrapolations	Transports based on standard distances of Ecoinvent. Infrastructure: proxy module used (chemical plant, organics)
Representativeness	UncertaintyAdjustments	none

73.10 References

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74 Sodium Chloride

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74.1 Introduction

Sodium chloride (NaCl, CAS-No. 7647-14-5) forms odorless cubic crystals. Depending on its degree of purity, the color varies between colorless when pure and white to gray when in the form of rock salt. Sodium chloride is very soluble in water. The most important chemical and physical properties are summarized in the following table. The description of reserves, resources and the use of salt are summarized from divers online information (Salt Institute (2002a), Salt Institute (2002b), Schweizer Rheinsalinen (2002), Salt Institute (2002c)) as well as from Westphal et al. (1993).

Synonyms for NaCl: Salt; Table salt; Saline solution; common salt; Sea Salt; Rock salt; halite

Tab. 74.1 Chemical and physical properties of Sodium Chloride (Salt Institute (2002a)).

Property	Value	Unit	Property	Value	Unit
Molecular weight	58.44	g mol ⁻¹	Melting point	801	°C
Density (at 25°C)	2.16	g cm ⁻³	Boiling point	1465	°C

74.2 Reserves and Resources

Sodium chloride can be found worldwide - either as mineral (called halite) most of it in underground deposits or as mixed evaporites in salt lakes. In Western Europe you can distinguish between about 7 different major salt basins - old between 40 and 250 Mio. years. Another source for sodium chloride is also seawater with about 2.7% (by weight) of NaCl. Even animals and humans contain small amounts of salt. Indeed, life and salt are interconnected due to the fact that salt is essential for life.

The annual salt production worldwide is in the order of 200 million tons. Therefrom, North America is producing more than a quarter, while Europe is producing about 20% of it. The biggest producer in Europe is Germany, followed by France and the United Kingdom. Relevant production sites are also situated in Italy, the Netherlands and Spain. Tab. 74.2 gives you an overview of the production in the most important countries of the world for the last ten years. Nowadays more than 100 countries have their own salt production sites.

Tab. 74.2 World sodium chloride production (in million metric tons, including salt in brine) from Salt Institute (2002c).

	USA	CAN	GER	FRA	U.K.	China	India	MEX	BRA	AUS	Others	Total
1990	37.0	11.3	15.7	6.6	6.4	20.0	9.5	7.1	5.4	7.2	45.6	183.0
1995	42.2	10.6	15.2	7.5	6.7	29.8	9.5	7.7	5.8	8.1	55.9	199.0
2000	45.6	11.9	15.7	7.0	5.8	31.3	14.5	8.9	6.0	8.8	58.5	214.0

In Switzerland there are two companies exploiting the different salt sources, "Vereinigte Schweizerische Rheinsalinen AG" and "Société Vaudoise des Mines et Salines de Bex". The sources in Switzerland extend over big parts of the northwestern part of the country, are aged of about 230 Mio. years and will continue to serve for another several centuries.

74.3 Production Technologies and Use

74.3.1 Production technologies for sodium chloride

For the production of dry salt, three different types of sodium chloride production can be distinguished namely, underground mining of halite deposits, solution mining with mechanical evaporation and solar evaporation. Their respective products are rock salt, evaporated salt and solar salt.

- **Underground mining:** The main characteristic of this technique is the fact that salt is not dissolved during the whole process. Instead underground halite deposits are mined with traditional techniques like undercutting, drilling and blasting or with huge mining machines with cutting heads. In a second step, the salt is crushed and screened to the desired size and then hoisted to the surface.
- **Solution mining and mechanical evaporation:** In this case, water is injected in a salt deposit, usually in about 150 to 500 m depth. The dissolution of the halite or salt deposits forms a cavern filled with brine. This brine is then pumped from the cavern back to the surface and transported to either an evaporation plant for the production of evaporated salt or transported directly to a chemical processing plant, e.g. a chlor-alkali plant. In Fig. 74.1, the schematic overview of such a solution mining together with evaporation step is shown.

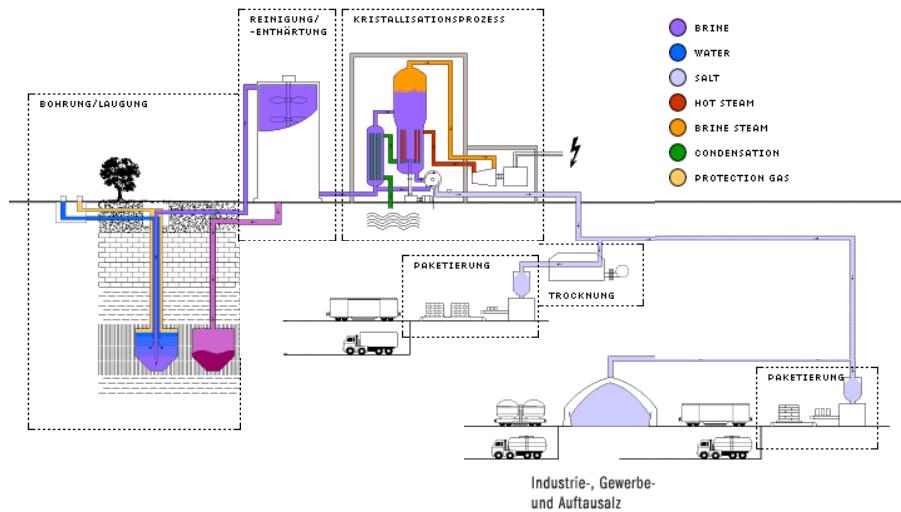


Fig. 74.1 schematic overview of the solution mining principle (graph from Schweizer Rheinsalinen (2002))

- **Solar evaporation:** In this case salt is produced with the aid of the sun and of wind out of seawater or natural brine in lakes. Within a chain of ponds, water is evaporated by sun until salt crystallizes on the floor of the ponds. Due to their natural process drivers such plants must be located in areas with only small amounts of rain and high evaporation rates - e.g. in the Mediterranean area where the rate between evaporation and rainfall is 3:1, in Australia even a ratio up to 15:1 can be found. There are some impurities due to the fact that seawater contains not only sodium chloride. That leads to impurities of calcium and magnesium sulfate as well as magnesium chloride. With the aid of clean brine from dissolved fine salt, these impurities are washed out.

As a forth form on the market you find the so-called "salt in brine", especially for the production of the different chemicals. In this case, the solution mining technique without an evaporation step afterwards is used. In 1996, 88% of the sodium chloride used in US chemical industry was salt in brine, and only 12% were dry salt. For Europe, similar information can not be found - for Germany a split of about 50:50 can be calculated for 1993 from the information in Verein Deutsche Salzindustrie e.V. (2002).

74.3.2 Use of sodium chloride

Sodium chloride has a huge variety of different uses. Up-to-now, more than 14'000 different uses are known worldwide. For example, salt is today the largest mineral feedstock consumed by the chemical industry. In the United States, chemical industry consumed in 1996 22.4 Mio metric tons of salt, representing about 42% of the total salt consumption. It is used as a chemical feedstock first of all for the production of chlorine and caustic soda in the chlor-alkali industry. Besides, you need also salt for the production of sodium chlorate and metallic sodium by electrolysis or for the production of sodium sulfate and hydrochloric acid by reacting sodium chloride with sulfuric acid.

Another very important area where sodium chloride is used is the human and animal nutrition. Because all animals, humans included, need both sodium and chloride. But, due to the fact that our body can produce neither of them, they are essential nutrients. Other relevant areas of use of salt are the maintenance and deicing of roads as well as the conditioning of water.

74.4 Systems characterization

In Europe, the possibilities for solar evaporation are rather poor and concentrated around the Mediterranean area. In 1996, less than 15% of the salt used came from solar evaporation plants, while rock mining and solution mining account for 44 resp. 42% (European Salt Producers' Association (2002)). Therefore, this study is focussing on the production of dry sodium chloride (by underground mining and by solution mining) as well as the salt brine production by solution mining. For the first case (dry salt) we use the above mentioned distribution between rock und solution mining, e.g. 51% rock salt und 49% solution mining.

74.5 Production of dry sodium chloride

74.5.1 Process data

Main data source is the information provided by a European salt producer. Additional sources (Habersatter (1991), Westphal et al. (1993), K+S AG (2002)) have been taken into account for plausibility checks and comparison reasons. Tab. 74.3 summarizes the quantitative information from the different sources.

Westphal et al. (1993) contains no quantitative information. The other data sources used show very different inputs and outputs. Therefore, the reflections resulting in the input and output data for this study are the following:

- **Energy demand:** Comparing the energy demand, a calculation of the total used energy shows a huge difference between K+S (0.048 kWh/kg) and Habersatter (0.234 kWh/kg), passing by the data from the European producer with 0.198 kWh/kg salt. The latter one states himself as representative for European salt production and therefore its value is used in this study. For the mix, as salt is produced almost in all European countries, an average mix from UCTE, Nordel and UK is used within this study.

Concerning the fuels, again the values from the European producer are used. As there is no information about the emissions from this producer, for light fuel oil not the fuel module but the heat module "heat, light fuel oil, at industry furnace 1MW (RER)" is used, as this module contains in addition also the process emissions. For similar reasons, the diesel input is shown by the module "diesel, burned in building machine (GLO)".

- **Material demand:** Due to the fact that K+S shows only a summarized consumption that is much higher and Habersatter has no material demand, the values from the European producer for NaOH and CaCO₃ are used within this study. The two packaging materials mentioned are not taken into account due to the fact, that - as shown in Fig. 74.1 - industrial salt is delivered as bulk.

Tab. 74.3 Production data of salt production (European producer: solution mining; K+S: solution mining and underground mining; Haberstatter: unknown)

[per kg salt]	European Producer	K + S	Habersatter	This study	remarks
Inputs					
Electricity	kWh	0.17		0.17	mix: see text ...
light fuel oil	g	4.63		4.63	heat module for light fuel oil
heavy fuel oil	g		6.50		
natural gas	m3		10.30		
hard coal	g		7.00		
diesel	g	0.10		0.10	module "diesel, burned in building machine"
Energy, Total	kWh		0.05		
CaO	g	13.88		13.88	
Na ₂ CO ₃	g	12.72		12.72	
Supply materials	g		275.86		
Auxiliary materials	g		1862.07		
packaging, PE	g	3.47			see text ...
packaging, cartonboard	g	4.63			see text ...
Water (process)	kg			3.82	Explication: see text ...
Water (cooling)	kg			2.69	Explication: see text ...
Water, Total	kg	6.51	1137.93	2.20	
Outputs					
NaCl	kg	1	1	1	
CO ₂ into air	kg		3.76		
CO into air	g	8.67	0.90		
NO _x into air	g		2.62		
SO _x into air	g		0.14		
Dust into air	g		0.45		
Construction waste	kg		0.24		
Waste (Recyclcng)	kg		0.41		
Waste (Disposed)	kg	0.03	0.28	0.04	0.03
Hazardous waste	g		32.76		
Residues	kg		77.86		
Waste water, total	kg		8.79		3.82 Explication: see text ...
Water (cooling)	kg		-	2.69	Explication: see text ...

- Water consumption:** From the solubility of NaCl in water, you can calculate a saturated solution using about 2.7 L water / kg NaCl (at 20 °C). A water consumption like mentioned in Habersatter is therefore too small for the solution mining proces (probably it is the underground mining process in Habersatter (1991)). Therefore, again, the value from the European producer is used. As this data source indicates only the total amount of water, a former questionnaire of the same producer (used for a confidential study at EMPA) containing separate values for process and cooling water is used for the calculation of the distribution. With this distribution the total value is then separated into the two fractions.
- Emissions to air and water:** From the European producer, no information about process specific emissions is available. The data in K+S are very specific for its own fuel mix and seems neither to include process-specific emissions. These air emissions from combustion, as already mentioned, are already included in the module "heat, light fuel oil". Additionally only the used electricity amount is visible as waste heat to air. The waste water is directly sent to a public waste water

treatment plant (WWTP). Due to a lack of further information, a composition similar to the average Swiss waste water is assumed.

- **Waste:** Impurities that are extracted together with sodium chloride are repumped into old caverns, like shown in Fig. 74.1. Thus they are not reported in the numbers above. For the additionally reported waste for disposal – due to the fact that no further information about the composition of this waste besides the fact that it contains CaSO_4 and CaSO_3 are known – the following waste module is used as a first approximation: "Disposal, decarbonising waste, 30% water, to residual material landfill".
- **Infrastructure and Transports:** From the different examined sources no information about specific infrastructure needs, nor about the transport amounts for the used materials is available. Therefore, the module "chemical plant, organics" having a built area of about 4.2 ha and an average output of 50'000 t/a is used as an approximation for the infrastructure. With a life-time of 50a, an amount of 4.0E-10 units/kg of sodium chloride is needed. For more details about this infrastructure module, see **chapter 2.7 in part I of this report**. For the transport of the input materials standard distances according to Frischknecht et al. (2003) are used.

74.5.2 Data quality considerations

Although representing a European average, the whole module is based on informations from just one solution mining site, estimating itself as representative for the whole industry. The uncertainty is estimated accordingly - especially as this module is representing a mix of solution mining and rock salt. Water in- and outputs have a higher uncertainty as these numbers are already the result of an estimation. As the infrastructure and the transports of the input materials are based on very rough estimation, their respective uncertainty is high.

The resulting data together with their respective uncertainty values for the dataset „sodium chloride, powder, at plant“ is shown in the following table. Additionally, the most important fields of the eco-spold meta information from those datasets are listed in chapter 74.9.

Tab. 74.4 In-/Outputs and uncertainty informations for the dataset "sodium chloride, powder, at plant"

Explanation	Name	Location	Unit	sodium chloride, powder, at plant	UncertaintyType	StandardDeviation95%	GeneralComment
				RER			
				0 kg			
Resources	Sodium chloride, in ground		kg	1.00E+00	1	1.58	(1.4,1,3,4,5); based on data from one solution mining site
Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.69E-03	1	1.6	(3,4,2,3,4,5); based on former information of one solution mining site
	Water, unspecified natural origin		m3	3.82E-03	1	1.6	(3,4,2,3,4,5); based on former information of one solution mining site
	quicklime, milled, loose, at plant	CH	kg	1.39E-02	1	1.58	(1,4,1,3,4,5); based on data from one solution mining site
	soda, powder, at plant	RER	kg	1.27E-02	1	1.58	(1,4,1,3,4,5); based on data from one solution mining site
	diesel, burned in building machine	GLO	MJ	4.28E-03	1	1.58	(1,4,1,3,4,5); based on data from one solution mining site
	heat, light fuel oil, at industrial furnace 1MW	RER	MJ	1.97E-01	1	1.58	(1,4,1,3,4,5); based on data from one solution mining site
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.70E-01	1	1.58	(1,4,1,3,4,5); based on data from one solution mining site
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); Estimation, based on Infrastructure of chemical production
	transport, lorry 32t	RER	tkm	2.67E-03	1	2.09	(4,5,n.a.n.a.n.a.n.a); standard distances
	transport, freight, rail	RER	tkm	1.60E-02	1	2.09	(4,5,n.a.n.a.n.a.n.a); standard distances
Waste	treatment, sewage, to wastewater treatment, class 4	CH	m3	3.82E-03	1	1.58	(1,4,1,3,4,5); based on data from one solution mining site
	disposal, decarbonising waste, 30% water, to residual material landfill	CH	kg	3.00E-02	1	1.58	(1,4,1,3,4,5); based on data from one solution mining site
Output	sodium chloride, powder, at plant	RER	kg	1			
Air emissions	Heat, waste		MJ	6.12E-01	1	1.58	(1,4,1,3,4,5); calculated from electricity consumption

74.6 Brine production

74.6.1 Process data

The production of brine is similar to the solution mining - but without the evaporation step afterwards. Only one source (Landbank (1994)) has specific data for this type of NaCl extraction. Additionally,

the above used data of the solution mining with evaporation from a European producer have been taken into account for plausibility checks and comparison reasons. Tab. 74.5 summarizes the data from these different sources together with the data used within this study.

Tab. 74.5 Production data of salt brine production (European producer: solution mining with evaporation; Landbank: brine pumping)

	[per kg salt]	European Producer	Landbank	This study
Inputs				
Salt rock	kg		1.13	1
Electricity	kWh	0.1734906	0.067	0.067
Heat	kWh		0.094	
light fuel oil	g	4.6342817		
heavy fuel oil	g			4.11E+00
natural gas	m3			4.66E-03
diesel	g	0.1		
CaO	g	7.5		
Na ₂ CO ₃	g	12.722646		
Water (process)	kg	0		3.82
Water (cooling)	kg	0		
Outputs				
NaCl	kg	1	1	1
Particulates	g		3.0E-01	
Heavy metals	g		2.0E-02	
Acids	g		8.0E-02	
Solid waste	kg	0.0346981	0.130	
Water (cooling)	m3	0		

First point is the missing water consumption in Landbank (1994), although it is clearly mentioned there that the data refer to the brine pumping process. Therefore, in this study, the value for process water from the European producer is used. We assume furthermore that no cooling water is used for in this process.

An input surplus of salt rock is only possible in the traditional underground mining extraction of salt - a pure solution mining has neglectable amounts of rock that is extracted (just during drilling of the wholes for the pumping). Westphal et al. (1993) indicates that the (underground) mining of brine is no longer widely used and therefore, we assume in this study that the brine originates from solution mining. Thus, the surplus salt rock input as well as its corresponding waste are neglectable. Usually, a brine that is used without a drying step is not purified from impurities and therefore, no auxillary materials are reported within this process. Concerning the energy demand, the values from Landbank (1994) are used, assuming a 50:50 split of the heat amount to heavy fuel oil and to natural gas. For the calculation of the amount of the two fuels, the low heating values according to Frischknecht et al. (2003) were used.

It is assumed that no further chemical products are used in this production process - the removal of impurities is made from the customer that purchases the brine solution.

In the emissions, the used electrical amount is visible as heat into air. Combustion emissions are not visible in this module, due to the fact that they are already included into the used heat modules ("heat, heavy fuel oil, at industrial furnace 1MW (RER)" and "heat, natural gas, at industry furnace >100kW (RER)"). Further air emissions are not taken into account. Concerning the waste water and its emissions, due to a lack of specific information, the same approach like for the sodium chlorine powder is used – with an average Swiss waste water that goes to a public waste water treatment plant.

Concerning the infrastructure - again the module "chemical plant, organics" is used as none of the used sources indicates anything about the infrastructure. Due to the fact that no auxillaries are used, no transport amounts have to be taken into account in this process.

74.6.2 Data quality considerations

The whole module is based on informations from one literature source as well as from a sodium chlorine powder production site - therefore this module has a higher uncertainty than the one for the powder form of NaCl. Water in- and output together with the infrastructure is based on rather rough estimation, their respective uncertainty is therefore high.

The resulting data together with their respective uncertainty values for the dataset „sodium chloride, brine solution, at plant“ is shown in Tab. 74.6. Additionally, the most important fields of the ecoinvent meta information from those datasets are listed in chapter 74.9.

Tab. 74.6 In/Outputs and uncertainty informations for the dataset "sodium chloride, brine solution, at plant"

Explanation	Name	Location	Unit	sodium chloride, brine solution, at plant			GeneralComment
				RER	o	uncertaintyType	
	Location	Infrastructure	Process Unit	kg		standardDeviation95%	
Resources	Sodium chloride, in ground		kg	1.00E+00	1	1.65	(3.5,3,3,4,5); based on 1 literature source
Input from Technosphere	Water, unspecified natural origin		m3	3.82E-03	1	1.65	(3.5,3,3,4,5); based on 1 literature source
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	1.69E-01	1	1.65	(3.5,3,3,4,5); based on 1 literature source
	heat, natural gas, at industrial furnace >100kW	RER	MJ	1.69E-01	1	1.65	(3.5,3,3,4,5); based on 1 literature source
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	6.70E-02	1	1.65	(3.5,3,3,4,5); based on 1 literature source
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); Estimation, based on infrastructure of chemical production

74.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

74.8 Conclusions

Average European datasets for the production of sodium chloride powder and brine solution for the year 2000 are established. Both datasets are in accordance with the present quality guidelines of the ecoinvent project. While the powder dataset is based on industry information, the latter dataset is based only on literature – thus has a higher uncertainty. Therefore, while the powder data are of good quality and can be used in a very broad context, the brine solution data can only give an approximation. They are not reliable enough for direct comparison of this material with alternative products..

74.9 EcoSpold Meta Information

ReferenceFunction	Name	sodium chloride, powder, at plant	sodium chloride, brine solution, at plant
Geography	Location	RER	RER
ReferenceFunction	InfrastructureProcess	0	0
ReferenceFunction	Unit	kg	kg
ReferenceFunction	IncludedProcesses	this module includes the solution mining process of sodium chloride, its cleaning form impurities, and the drying step. It is sold as bulk and therefore no packaging materials are included.	this module includes the solution mining process of sodium chloride for the preparation of a brine for industrial use. No cleaning or drying step are therefore included.
ReferenceFunction	Amount	1	1
ReferenceFunction	LocalName	Natriumchlorid, Pulver, ab Werk	Natriumchlorid, Brine- Lösung, ab Werk
ReferenceFunction	Synonyms	Steinsalz//salt//Salz	Salzlösung//salt solution
ReferenceFunction	GeneralComment		
ReferenceFunction	CASNumber	7647-14-5	7647-14-5
TimePeriod	StartDate	2000	1994
TimePeriod	EndDate	2000	1994
TimePeriod	DataValidForEntirePeriod	1	1
TimePeriod	OtherPeriodText		data of publication of the used literature source
Geography	Text	data from one European solution mining site - used to represent the European mix of 41% solution mining and 59% rock salt	estimation, based on one European literature source - valuable for european situation
Technology	Text	modern solution mining technology (thermo compressing technology)	modern solution mining technique (mix)
Representativeness	Percent		
Representativeness	ProductionVolume	ca. 40 Mio. t	unknown
Representativeness	SamplingProcedure	questionnaire from one European solution mining site	literature data
Representativeness	Extrapolations	see geography	see geography
Representativeness	UncertaintyAdjustments		

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75 Sodium dichromate

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75.1 Introduction

This chapter describes the production of sodium dichromate. This chemical is used primarily for pigment manufacturing, leather tanning, metals treating and other application.

75.2 Reserves and resources of sodium dichromate

Sodium dichromate is an inorganic chemical compound. It is produced from chromite ore.

75.3 Characterisation of sodium dichromate

Sodium dichromate is available as an orange liquid solution or as red-orange crystals. Its chemical formula is $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. Anhydrous sodium dichromate (bichromate in the US) is highly soluble in water. It is an oxidizing agent and reacts with a variety of other chemicals. Sodium dichromate may react explosively with other chemicals to sustain fire.

Tab. 75.1 Physical characteristics of sodium dichromate (Elementis Chromium)

Molecular weight	2.98 g / mol
Chromium content by weight	43.3%
Loses water of crystallization	82.6 °C
Anhydrous salt melts at	357 °C
Salt decomposes at	400 °C

Sodium dichromate contains hexavalent chromium, making it a cancer hazard. The anhydrous crystals can be fatal if ingested and can cause cancer by inhalation. (Elementis Chromium MSDS)

75.4 Production and use of sodium dichromate

In 1997, US demand was 141'000 tonnes. 1.8% annual growth was expected until 2001. No figures were readily available for Europe. Elementis Chromium is the world's largest producer of chromium chemicals, with plants in the US and the UK.

Tab. 75.2 1997 uses of sodium dichromate (EPA Dichromate, 2000)

Chromic acid	66%
Leather tanning	13%
Chromic oxide	9%
Pigments	6%
Others (wood preservatives, paints)	6%

Chromic acid is used to produce resistant coating for a variety of base metals.

It is also used in the metal finishing industry to produce resistant coatings for a variety of base metals. Other uses include decorative plating, conversion coatings, and metal coloring compounds.

Sodium dichromate is used to make tanning compounds for the leather tanning industry.

In the pigment industry, sodium dichromate is used to manufacture lead chromate compounds, which are then used in manufacturing paints, printing inks, and floor coverings. Chromic green oxide, another sodium dichromate derived pigment, is resistant to light, heat, acids and alkalis and is used in rubber, roofing, ceramics and chemical-resistant paints. Sodium dichromates are also used in textile dying operations or in the production of the textile dyes themselves.

75.5 System characterization

The starting material for sodium dichromate is the ore chromite, which consists of approximately 50% Cr₂O₅, the rest being mostly iron oxide, aluminium oxide, silicium oxide and magnesium oxide. The ore is imported (e.g. from South Africa) and ground.

Two different processes are described in the available literature on sodium dichromate manufacturing.

75.5.1 Electrolytic process ⁴

The chromite is mixed with limestone and soda ash (sodium carbonate), and then roasted as about 1200 °C. This oxidizes the mostly trivalent chromium to hexavalent chromium. An air pollution control system on the hearth system sends captured residues directly to a weak chromate solution. The hexavalent chromium is leached with hot water to separate the soluble sodium chromate (Na₂CrO₄). The sodium chromate is purified and is then converted electrolytically to sodium dichromate. Hydrogen and oxygen, which are produced during electrolysis, are vented to the atmosphere.

During electrolysis, a sodium hydroxide solution is produced, which is treated with ferrous chloride and sold.

75.5.2 Sulfuric acid process ⁵

Roasting of sodium chromite is accomplished with soda ash and limestone. Sodium chromate is produced, as well as carbon dioxide emissions (1). The sodium chromate is treated with sulphuric acid and sodium carbonate to produce dichromate and sodium sulfate (2). The dichromate solution is neutralized to filter the remaining ore residues, which precipitate, then fed to a crystallizer, then to a centrifuge and drier. The post-neutralisation residues are sent to a treatment facility.

Sodium sulfate (saltcake) from the sodium dichromate solution is sold as a sulfur source for the Kraft Paper manufacturing process.



75.6 Life cycle Inventory for sodium dichromate

Somewhat complete information is only available for the sulphuric acid process. No information was made available for the electrolytic process.

⁴ Referred to in (EPA Dichromate, 2000) as The Elementis Chromium, LP facility production process

⁵ referred to in (EPA Dichromate, 2000) as the OxyChem manufacturing process

75.6.1 Precursor materials (sulphuric acid process)

Tab. 75.3 precursors for dichromate production (Chromium, 1998)

Consumption per ton of product	Amount (tons)
Chromium (in ore)	0.51
Chromite ore	1.64
Sodium carbonate	1.0
Sulfuric acid	0.41
limestone*	1.21

* some unconverted chromite ore is also included in this figure

This process produces 0.6 tons of sodium sulfate (salt cake) per ton of sodium dichromate. Based on market prices x mass for both products, it was determined that less than 4% of the environmental load can be allocated to the sulfate. This is too little to have a marked effect and for this reason, the entire environmental burden is allocated to the dichromate.

Tab. 75.4 Allocation factors for dichromate production (Chromium, 1998)

	Saltcake	Dichromate	Remarks
Price	USD 82 / ton according to (CMR11-25-02)	0.6 USD / lb according to Chemical Profiles	
Amount	0.61 tonnes	1 tonne	1 tonne = 2200 lb
Price x amount (%)	3.65	96.35	

75.6.2 Energy usage (sulphuric acid process)

Tab. 75.5 Energy usage for dichromate production (Chromium, 1998)

Consumption per ton of product	Amount
Fuel gas (natural gas)	303 cubic meters
Fuel mix for steam production	12.8 GJ
Electricity (MWh)	0.18

75.6.3 Air emissions (sulphuric acid process)

According to Chromium (1998), 1.25 kg of CO₂ are emitted per kg of product, as well as 0.3 kg of dust. Assuming the dust figure is pre-treatment, air pollution control devices with an efficiency of 99% would reduce the dust to 0.003 kg / kg product.

75.6.4 Wastewater emissions (EPA Dichromate, 2000)

Electrolytic process: The sodium dichromate crystallization, evaporation and drying unit generates wastewater, which is fed to an onsite wastewater treatment unit. The wastewaters are treated with sodium sulfide solution to reduce hexavalent chromium to trivalent chromium and with sulfuric acid to adjust the pH. Total chromium content is 0.5 mg/kg. The wastewater settles and dewatered. The sludge is landfilled, the effluent is filtered and discharged to a shipping channel. The total amount of hexavalent chromium released, in 1998 was 0.003 tonnes (MT). (EPA Dichromate, 2000), Chapter 2.3.7.

Based on 1998 production, which assumes a growth rate of 1.8% from 1997 onwards, it can be estimated that 0.06 mg of hexavalent chromium exits the plant per kg of produced sodium dichromate. Total trivalent chromium release was 0.08 tonnes, which relates to 1.5 g chromium (III) per kg product.

Sulfuric acid process: The total amount of hexavalent chromium released, in 1998 was nil (EPA Dichromate, 2000), Chapter 3.3.6. The facility was, however, permitted to release up to 51 kg a year. Based on the production figures in (EPA Dichromate, 2000) Table 1.2, it can be estimated that 0.47 mg hexavalent chromium is permitted to exit the plant per kg of produced sodium dichromate. Total chromium discharges were permitted up to 450 kg per year. Taking production information into account, this amounts to 4 mg chrome (III) emissions per kg of produced sodium dichromate.

75.6.5 Liquid wastes

No liquid wastes are given.

75.6.6 Solid wastes (EPA Dichromate, 2000)

Electrolytic process. Residual waste has a total chromium concentration of 20 mg/kg. The waste consists of 20% moisture and 80% solids. The waste does not contain any volatile constituents of concern.. Waste is landfilled. In 1997, a total of 49'900 tonnes of sodium dichromate was produced at the facility described in (EPA Dichromate, 2000), Table 1.2. Assuming a 1.8% growth rate, this amounts to 50'800 tonnes in the following year. According to (EPA Dichromate, 2000), Table 2.2, total chromium contribution to the landfill (a surface impoundment) was 6,540,000 kg in 1998. This amounts to 128.7 kg of elemental chromium disposed of per ton of sodium dichromate. The waste is referred to as “reduced chromium treatment residues” and consists of trivalent chromium wastes, mostly spent post-neutralization ore residues.

Sulfuric acid process: Wastes are treated with ferrous chloride reducing agent to reduce hexavalent chromium to trivalent chromium. Based on the total estimated chromium contribution to the disposal site of 5'880 tonnes (EPA Dichromate, 2000), Tables 1.2 and 3.5, it can be estimated that 1.2 kg of solid wastes or 55 g of elemental chromium is disposed of per kg of sodium dichromate. These wastes are referred to as reduced chromium treatment residues; they consist of 4.5 wt % chromium (III).

Tab. 75.6 Main components of reduced chromium treatment residues (EPA Dichromate, 2000: Table 3.3)

Chemical component	Amount (%)
Chromium (III)	4.54
Iron	21.4
Aluminium	9.9
Calcium	9.1
Magnesium	4.8

75.6.7 Infrastructure and transports

No information was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.000000004 units per kg of produced dichromate.

Transport information is taken from the chapter “Chromium” in Althaus et al. (2003). The transports used are 12'600 tkm ocean freighter, 985 tkm rail transport and 76 tkm truck (per ton of chromite ore).

Standard distances and means according to Frischknecht et al. (2003) are used for all remaining materials.

75.7 Data quality considerations

The data quality is considered to be poor, as no information is available for the electrolytic process. The inputs of raw materials are approximate, and the emissions are incomplete. The inventory is based on the sulphuric acid process. The wastewater emissions of chromium (VI) are not considered to be nil, as in the base year for (EPA Dichromate, 2000), but are taken from EPA's maximum permitted effluent amount. The reasons for this are a) the electrolysis process also emits chromium (VI) wastewater emissions and b) it cannot be assumed that the sulphuric acid process never emits chromium (VI) emissions, as there are several facilities located worldwide.

The following table summarizes the input and output data as well as the uncertainties used for the production of sodium dichromate. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 75.10.

Tab. 75.7 Input / output data and data quality for dichromate production in Europe

Explanation	Name	Location	Unit	sodium dichromate, at plant		UncertaintyType	StandardDeviation95%	GeneralComment			
				RER							
				kg							
Input from Technosphere	chemical plant, organics	RER	unit	4.00E-10	1	1.32	(4,5,1,1,1,4); infrastructure				
	chromite, ore concentrate, at beneficiation	GLO	kg	1.64E+00	1	1.12	(1,3,1,1,1,4); chromite ore				
	disposal, residues Na-dichromate prod., 0% water, to residual material landfill	CH	kg	1.20E+00	1	1.12	(1,3,1,1,1,4); residues				
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.80E-01	1	1.12	(1,3,1,1,1,4); power				
	heat, natural gas, at industrial furnace >100kW	RER	MJ	1.12E+01	1	1.12	(1,3,1,1,1,4); fuel				
	heat, unspecific, in chemical plant	RER	MJ	1.28E+01	1	1.24	(4,3,1,1,1,4); steam production				
	limestone, milled, loose, at plant	CH	kg	1.21E+00	1	1.12	(1,3,1,1,1,4); ancillary material				
	soda, powder, at plant	RER	kg	1.00E+00	1	1.12	(1,3,1,1,1,4); soda				
	sulphuric acid, liquid, at plant	RER	kg	4.10E-01	1	1.12	(1,3,1,1,1,4); ancillary material				
	transport, freight, rail	RER	tkm	3.19E+00	1	1.24	(4,3,1,1,1,4); transport				
	transport, lorry 32t	RER	tkm	3.87E-01	1	1.24	(4,3,1,1,1,4); transport				
	transport, transoceanic freight ship	OCE	tkm	2.07E+01	1	1.24	(4,3,1,1,1,4); transport				
air emission	Carbon dioxide, fossil		kg	1.25E+00	1	1.12	(1,3,1,1,1,4); emission				
	Heat, waste		MJ	6.50E-01	1	1.12	(1,3,1,1,1,4); waste heat				
	Particulates, > 2.5 um, and < 10um		kg	3.00E-03	1	1.12	(1,3,1,1,1,4); emission				
water emission	Chromium VI		kg	4.70E-07	1	1.12	(1,3,1,1,1,4); wastewater emission				
output	Chromium, ion		kg	4.00E-06	1	1.12	(1,3,1,1,1,4); wastewater emission				
	sodium dichromate, at plant	RER	kg	1							

75.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

75.9 Conclusions

The inventory for sodium dichromate is based on industry sources, estimations and assumptions representing just one possibility of production. The unit process raw data are meant to be used as background information if sodium dichromate is used for a product in small amounts. Therefore these data can only give a rough approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

75.10EcoSpold Meta Information

ReferenceFunction	Name	sodium dichromate, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Included are the raw material, as well as the energy and auxillaries input are taken into account togehter with air emissions and waste. Transports and infrastructure are estimated. No water emissions are taken into account.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Natriumdichromat, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	Sodium dichromate, produced by the sulfuric acid process. The electrolysis production process is not included here, therefore the data quality is considered poor.
ReferenceFunction	CASNumber	10588-01-9
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	Average European Values
Technology	Text	based on literature data on the acidification process, taken from plant data in Europe and North America
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	see technology and generalComments
Representativeness	UncertaintyAdjustments	none

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76 Sodium hypochlorite

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76.1 Introduction

This chapter describes the production of sodium hypochlorite (NaOCl). In Western Europe, sodium hypochlorite is used primarily for household sanitizing and bleaching solutions as well as for water treatment (pools). (SRI hypochlorite)

Synonyms for sodium hypochlorite: soda bleach, liquid bleach

76.2 Reserves and resources of sodium hypochlorite

Sodium hypochlorite is an inorganic compound. It is produced by reacting dilute caustic soda solution with liquid or gaseous chlorine.

76.3 Characterisation of sodium hypochlorite

Sodium hypochlorite (NaOCl), CAS 7681-52-9, is a pale yellow-greenish liquid with a chlorine odor. It boils at 120 °C and freezes at 8.6 °C. Its concentration in water is 5-7%, based on available chlorine. NaOCl is soluble in cold water, but decomposes in hot water. NaOCl is a corrosive, oxidizing agent. Its solutions can slowly produce burns when in contact with the skin. Inhalation may cause burns on mouth, throat and stomach. (Inchem naocl)

76.4 Production and use of NaOCl

In Western Europe, sodium hypochlorite is used primarily for household sanitizing and bleaching solutions, water treatment (including pools) and chemical production. Household use accounts for 40% of total use, on a chlorine-equivalent basis. In the United States, HOCl is mostly used for household laundry and disinfection and for industrial bleaching and sanitation, as well as for swimming pool sanitation. (SRI hypochlorite).

Total US annual capacity for household sodium hypochlorite solution (5.25 % NaOCl) is estimated to be 3.78 billion liters. Total US annual capacity for industrial sodium hypochlorite solution (12.5 % NaOCl) is estimated to be 5.86 billion liters, (Chemical Profiles)

Producers include Solvay, PPG Industries and many small- and midsize companies..

76.5 System characterization

NaOCl is prepared by reacting dilute caustic soda solution with liquid or gaseous chlorine. The reaction mixture is cooled, as the reaction is exothermic.



The resulting solution is stabilized by adjusting the pH-value. The yield is nearly 100% of the theoretical value based on chlorine, according to industry sources.

76.6 Life cycle Inventory for NaOCl

This report assumes that NaOCl is generated from chlorine process emissions. The chlorine precursor does therefore not carry any environmental burden. However, the caustic used to capture the chlorine is accounted for, as is the thermal and electrical energy.

76.6.1 Precursors

Tab. 76.1 precursors per kg 100% NaOCl (industry sources)

Input	kg
Caustic soda (50%)	1.12
Chlorine	0.95

76.6.2 Energy consumption

Tab. 76.2 energy consumption per kg NaOCl (industry sources)

	Steam	Power
steam	0.5 kg	0.017 kWh

76.6.3 Air emissions

no information available

76.6.4 Wastewater emissions

It is assumed that sodium chloride is discharged (0.78 kg per kg product), calculated from the inputs via molecular weights.

76.6.5 Liquid wastes

no information available

76.6.6 Solid wastes

no information available

76.6.7 Transports and infrastructure

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.000000004 units per kg of produced sodium hypochlorite (NaOCl).

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2003) are used for the different raw materials.

76.7 Data quality considerations

The data quality is considered to be fair, as few emissions are to be expected from this process.

The following table summarizes the input and output data as well as the uncertainties used for the production of 1 kg hypochlorite. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 76.10.

Tab. 76.3 Input / output data and data quality for production of 1 kg hypochlorite (100%)

Explanations	Name	Location	Unit	sodium hypochlorite, 15% in H ₂ O, at plant	Uncertainty Type	Standard Deviation 95%	General Comment
	Location			RER			
	Infrastructure Process			0			
	Unit			kg			
Input from Technosphere	chemical plant, organics	RER	unit	4.00E-10	1	1.32	(4,5,1,1,1,4); infrastructure
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.70E-02	1	1.12	(1,3,1,1,1,4); power
	heat, unspecific, in chemical plant	RER	MJ	1.38E+00	1	1.24	(4,3,1,1,1,4); steam production
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	5.60E-01	1	1.12	(1,3,1,1,1,4); precursor
	transport, freight, rail	RER	tkm	1.24E+00	1	1.24	(4,3,1,1,1,4); transport
	transport, lorry 32t	RER	tkm	2.10E-01	1	1.24	(4,3,1,1,1,4); transport
water emission	Chloride	-	kg	4.80E-01	1	1.24	(4,3,1,1,1,4); wastewater
air emission	Heat, waste	-	MJ	6.00E-02	1	1.12	(1,3,1,1,1,4); waste heat
Outputs	sodium hypochlorite, 15% in H ₂ O, at plant	RER	kg	1			

76.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

76.9 Conclusions

The inventory for sodium hypochlorite is based on industry sources, estimations and assumptions. The dataset is in accordance with the present quality guidelines of the ecoinvent project. The data are thus of a reasonable quality and can be used in quite a broad context.

76.10 EcoSpold Meta Information

ReferenceFunction	Name	sodium hypochlorite, 15% in H ₂ O, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	includes all precursor compounds except for chlorine, which is treated as process air emissions, transports and infrastructure
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Natriumhypochlorit, 15%in H ₂ O, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	Production of NaOCl from chlorine emissions captured in 50% sodium hydroxide solution.
ReferenceFunction	CASNumber	7681-52-9
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	RER
Technology	Text	based on literature data and plant data in Europe and North America
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	see GeneralComment
Representativeness	UncertaintyAdjustments	none

76.11 References

- Chemical Profiles Chemical profiles are published weekly in the Chemical Market Reporter, a publication of the Schnell Publishing Company, a member of the Reed Elsevier group
- Frischknecht et al. (2003) Frischknecht R., Althaus H.-J., Doka G., Dones R., Hischier R., Hellweg S., Jungbluth N., Kellenberger D., Nemecek T., Rebitzer G. and Spielmann M. (2003b) Overview and Methodology. Final report ecoinvent 2000 No. 1. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.
- Inchem naocl <http://www.inchem.com.ph/naocl.htm>
- SRI hypochlorite Abstract of CEH Report Hypochlorite Bleaches, SRI Consulting,. available on <http://ceh.sric.sri.com/Public/Reports/508.2000/Abstract.html>

77 Sodium sulfite

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Review: Heiko Kunst, TU Berlin

77.1 Introduction

This chapter describes the production of sodium sulfite (sulfite, at plant). This chemical is used primarily as a pulping agent and dechlorination agent by the paper industry.

Synonyms for sodium sulfite: Santosite, sulfurous acid, disodium salt

77.2 Reserves and resources of sodium sulfite

Sodium sulfite is an inorganic chemical compound. It is produced from sulfur dioxide.

77.3 Characterisation of sodium sulfite

Anhydrous sodium sulfite is a white crystalline solid. It is also available as a clear, colorless aqueous solution (15-20%). Its chemical formula is Na_2SO_3 . Sodium sulfite is soluble in water and glycerol. It is not soluble in acetone or alcohol. Ingestion of sodium sulfite may prove fatal. Sodium sulfite is non-combustible. (Data stem from Material Safety Data Sheets of various producers)

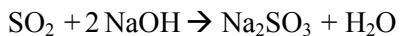
77.4 Production and use of sodium sulfite

US demand 2000: 102 thousand tonnes; 2004: 106 thousand tonnes, projected according to Chemical Profiles published in the Chemical Market Reporter. No figures were readily available for Europe.

Sodium sulfite is primarily used as a pulping agent and dechlorination agent by the paper industry. Other applications include its use to remove oxygen in boiler water and as an antioxidant in film processing. Sodium sulfite also serves to remove chlorine after bleaching of wood pulp.

77.5 System characterization

Sodium sulfite is manufactured by absorbing sulfur dioxide gas (SO_2) in an alkaline solution. The alkali can be calcium carbonate or sodium hydroxide. The SO_2 can be produced either by burning sulfur or from desulfurization of power plant flue gas. By controlling pH and the operating mode of the crystallizer, sodium sulfite is produced. A crystallizer is used to boil the solution and form crystals. Finally the crystals are removed, centrifuged and dried. (Information compiled from web sites of various producers).



77.6 Life cycle Inventory for sodium sulfite

The following information was developed from industry sources and is based on the use of caustic instead of calcium carbonate.

77.6.1 Precursor materials

Sulfur dioxide, 0.51 kg

Sodium hydroxide, 50% solution, 1.28 kg

77.6.2 Energy usage

Tab. 77.1 Energy usage for sodium sulfite production (industry sources)

Consumption per kg of product	[MJ]
Steam	2.3
Electricity	1

77.6.3 Air emissions

No information available

77.6.4 Wastewater emissions

No information available

77.6.5 Liquid wastes

No liquid wastes are given.

77.6.6 Solid wastes

No information available

77.6.7 Infrastructure and transports

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.000000004 units per kg of produced sulfite.

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2003) are used for the different raw materials.

77.7 Data quality considerations

The data quality is considered to be poor, as the raw materials and energy usage are estimated from industry sources and only one production process is considered. No information was given on emissions.

The following table summarizes the input and output data as well as the uncertainties used for the production of sodium sulfite. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 77.10.

Tab. 77.2 Input / output data and data quality for sulfite production in Europe

Explanations	Name	Location	Unit	sulphite, at plant	Uncertainty Type	Standard Deviation 95%	General Comment
	Location			RER			
	Infrastructure Process			0			
	Unit			kg			
Input from Technosphere	chemical plant, organics	RER	unit	4.00E-10	1	1.22	(2,2,1,3,1,5); infrastructure
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	2.80E-01	1	1.68	(4,5,1,3,4,5); electricity
	heat, unspecific, in chemical plant	RER	MJ	2.30E+00	1	1.68	(4,5,1,3,4,5); heat
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	6.40E-01	1	1.68	(4,5,1,3,4,5); precursor
	sulphur dioxide, liquid, at plant	RER	kg	5.10E-01	1	1.68	(4,5,1,3,4,5); precursor
	transport, freight, rail	RER	tkm	7.62E-01	1	1.31	(4,3,1,2,1,5); transport
	transport, lorry 32t	RER	tkm	1.27E-01	1	1.31	(4,3,1,2,1,5); transport
Emissions Outputs	Heat, waste	-	MJ	1.00E+00	1	1.30	(4,2,1,2,1,5); emission
	sulphite, at plant	RER	kg	1			

77.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

77.9 Conclusions

The inventory for sodium sulfite is based on industry sources, estimations and assumptions. The unit process raw data are meant to be used as background information if sodium sulfite is used for a product in small amounts. Therefore these data can only give a rough approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

77.10 EcoSpold Meta Information

ReferenceFunction	Name	sulphite, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	includes precursors, transports and infrastructure
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Sulfit, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	This inventory is based on industry sources and is meant as a rough approximation. Precursors, transports and infrastructure are included.
ReferenceFunction	CASNumber	14265-45-3
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	RER
Technology	Text	represents a current cross-section of actual plants in Europe
Representativeness	Percent	
Representativeness	ProductionVolume	
Representativeness	SamplingProcedure	
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

77.11 References

- Chemical Market Reporter a publication of the Schnell Publishing Company, a member of the Reed Elsevier group
- Frischknecht et al. (2003) Frischknecht R., Althaus H.-J., Doka G., Dones R., Hischier R., Hellweg S., Jungbluth N., Kellenberger D., Nemecek T., Rebitzer G. and Spielmann M. (2003b) Overview and Methodology. Final report ecoinvent 2000 No. 1. Swiss Centre for Life Cycle Inventories, Dübendorf, CH, Online-Version under: www.ecoinvent.ch.
- Solvay MSDS Material Safety Data Sheet, Solvay Minerals, inc., USA, April 2002

78 Sodium sulphate

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 Review: Heiko Kunst, TU Berlin

78.1 Introduction

Sodium sulphate (Na_2SO_4 , CAS-No. 7757-82-6) is a naturally occurring mineral, called thenardite (anhydrous form) resp. Glauber's salt (decahydrate form – i.e. $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$). Besides the minerals, sodium sulphate is also produced chemically – either as a by-product of other processes or as the main product of a process (von Plessen (1993)). As Glauber's salt is not a commercial product according to von Plessen (1993), for the ecoinvent project, only the anhydrous form of sodium sulphate is further examined. The most important chemical and physical properties of the form of sodium sulphate used in this inventory are given below.

Synonyms: Disodium sulfate; Sulfuric acid, sodium salt; Sulfuric acid, disodium salt

Tab. 78.1 Chemical and physical properties of sodium sulphate (according to von Plessen (1993))

Property	Unit	Value	Remarks
Molecular weight	142.04	g mol^{-1}	
Melting point	884	$^{\circ}\text{C}$	at normal pressure
Density	2.697	g cm^{-3}	at normal pressure

78.2 Production, Reserves and Resources of Material

Of the worldwide production of sodium sulphate – according to Kostick (1997) 5.52 Mt in 1997 – around 65% are of natural origin and the other 35% are produced in the chemical industry. According to von Plessen (1993), and based on data for 1988, natural origin and chemical origin are quite equal.

The most important production places for natural occurring sodium sulphate are Canada, Spain, Mexico, Turkey, the United States and Russia. According to Kostick (1997), the natural resources of sodium sulphate will last for hundreds of years with the present exploitation rate.

78.3 Use of Material / Product

According to Kostick (1997), the consumption of sodium sulphate in the United States in the Mid 90's was about 42% for soap and detergents, 15% for textiles, 12% for pulp and paper, 11% for glass and the remaining 20% for a variety of other uses – e.g. carpet fresheners or starch manufacturing.

In von Plessen (1993), describing Western World conditions, again the detergent industry is shown as the most important consumer, followed by the cellulose industry and the glass production.

78.4 Systems Characterization

Within this dataset, three different origins of sodium sulphate are distinguished: natural origins, production as a by-product and production as a main product. The split to these three types of origins is made based on the information given above – assuming 60% natural, 25% by-product and 15% main product. For each of these three types, the following characteristics are used:

- **Natural:** For the exploitation of naturally occurring sodium sulphate, the energy consumption as well as the emissions to water are estimated based on similar processes. Thus, this module represents not more than a rough estimation.
- **By-product:** No environmental burden for the material is taken into account, as this is a by-product of another production process. Energy consumption for the conditioning is estimated. Thus, this module is not more than a very rough estimation.
- **Main product:** In the production process for chemically produced sodium sulphate the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements.

For this inventory the functional unit is 1 kg of anhydrous solid sodium sulphate mix. Due to the fact, that all three production ways are not very detailed documented, the mix module again is not more than a rough estimation – a process that should be used only for processes where the impact of sodium sulphate is not considered to be high. As process location Europe (RER) is used.

78.5 Sodium sulphate, from natural sources, at plant (Location: RER)

This dataset includes a rough estimation of the exploitation process of naturally occurring sodium sulphate. According to von Plessen (1993), a variety of different processes are used for the production of sodium sulphate from natural resources. Several of these processes use shallow basins, where water is evaporated naturally during hot weather. In a second step, the precipitated minerals containing sodium sulphate are then taken off these basins for further treatment. Another possibility is the use of floating dredges for the mining of permanent deposits of sodium sulphate containing rock.

No data were available within the ecoinvent project for any type of exploitation of natural sources of sodium sulphate. Thus, the following assumptions are used:

- The overall yield for the sodium sulphate minerals is assumed to be 95% - thus per kg of sodium sulphate, from natural resources, 1.05 kg of sodium sulphate minerals is needed
- For the first step (evaporation of water from a brine of sodium sulphate minerals) no environmental burdens are taken into account
- For the further treatment, the energy consumption is approximated by the energy consumption for the sodium chloride production (see chapter XY of this report). Besides the energy, no further input is taken into account. Concerning emissions to air and water, it is assumed here that 50% of the surplus input of sodium sulphate is eliminated in the water and 50% are eliminated within the inert waste that is assumed to be landfilled.
- Infrastructure & Transport: As no specific information is available, the unspecified dataset “chemical plant, organics” is used – but due to the fact that here only little infrastructure is needed, only half of the amount compared with other chemicals is used here. As there are no other materials besides the mineral no transport is taken into account within this dataset.

All in all, this results in the data summarized in Tab. 78.2.

Tab. 78.2 Energy demand, Resource demand and emissions for the production of sodium sulphate out of naturally occurring sodium sulphate deposits

[per kg sodium sulphate]				Remark
INPUTS				
sodium sulphate, in ground	kg	1.053	overall yield of 95% assumed	
Electricity, medium voltage	kWh	1.70E-01	estimated, based on NaCl production	
Light fuel oil, burned in industrial furnace	MJ	1.91E-01	estimated, based on NaCl production	
Diesel, in construction machine	MJ	4.28E-03	estimated, based on NaCl production	
chemical plant, organics	unit	2.00E-10	approximation for infrastructure	
OUTPUTS				
sodium sulphate	kg	1	product	
waste heat, to air	MJ	6.12E-01	calculated from electricity input	
sulphate, to water	kg	2.58E-02	estimated as 50% of surplus input	
waste (landfilling)	kg	3.00E-02	containing the remaining surplus input	

78.6 Sodium sulphate, Mannheim process, at plant (Location: RER)

78.6.1 Process

This dataset includes a rough estimation of the production process for sodium sulphate according to the so-called Mannheim process. Due to missing production data this inventory bases on stoichiometric calculations. The emissions to air and water were estimated using mass balance. It was assumed that the waste water is treated in a internal waste water treatment plant. Data about the energy and water consumption are taken from von Plessen (1993).

The mentioned production way for sodium sulphate, can be summarized within the following overall stoichiometric reaction equation:



78.6.2 Resources

Raw materials and Chemicals

According to the above shown final reaction equation - the following stoichiometric inputs are needed (yield 100%) for the production of 1.0 kg of sodium sulphate:

- sodium chloride, NaCl: 822.867 g (14.081 mol)
- sulphuric acid, H₂SO₄: 690.439 g (7.040 mol)

For the production a yield of 95% for the overall reaction is assumed. Therefore 866.176 g sodium chloride and 726.778 g sulphuric acid (100%) are considered as raw materials in this inventory. A summary of the values used is given in Tab. 78.3.

Energy

According to von Plessen (1993) the production of 1 t of sodium sulphate uses $3.6 * 10^6$ kJ heat (according to this literature source, this equals 88 kg fuel oil) and 65 kWh electricity. For the ecoinvent project a mix for the heat fuel of 50% heavy fuel oil and 50% natural gas is assumed. A summary of the values used is given in Tab. 78.3.

Water use

According to the same source, the water consumption per t of sodium sulphate is in the order of 1.4 m³ process water and 26 m³ cooling water. For the process water, the “unspecified” module is used due to a lack of further information.

Transport and Infrastructure

As there is no information about the transport amounts, standard distances and means according to Frischknecht et al. (2003) are used for the different raw materials.

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg sodium sulphate was included.

78.6.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed, i.e. 0.234 MJ per kg sodium sulphate is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of sodium sulphate. Thus, as a first approximation, an amount of 0.2% of sulphuric acid is used for this dataset here. This assumption leads to air emissions of 1.454 g sulphuric acid.

Emissions to water

The remaining amount of un-reacted raw materials was assumed to leave the production process with the wastewater. This assumption leads to a pollution of the waste water with 43.309 g sodium chloride and 34.885 g sulphuric acid per kg product.

Both substances are not taken off the water in a waste water treatment plant (WWTP) – thus, the water emissions are 17.045 g sodium ions, 26.264 g chloride ions and 34.174 g sulphate. DOC, TOC, COD and BOD are assumed to be zero as this reaction doesn't contain any organic substances. A summary of the values used in this inventory is given in Tab. 78.3.

Solid wastes

Solid wastes occurring during the production of sodium sulphate were neglected in this inventory.

Tab. 78.3 Energy demand, Resource demand and emissions for the Mannheim process

[per kg sodium sulphate]			Remark
INPUTS			
sodium chloride	kg	0.866	stoichiometric calc., yield 95%
sulphuric acid	kg	0.727	stoichiometric calc., yield 95%
Water, unspecified	m3	0.001	according to von Plessen 1993
Water, cooling, unspecified	m3	2.60E-02	according to von Plessen 1993
Electricity, medium voltage	kWh	6.50E-02	according to von Plessen 1993
Natural gas, burned in industrial furnace >100kW	MJ	1.80E+00	according to von Plessen 1993
Heavy fuel oil, burned in industrial furnace	MJ	1.8	according to von Plessen 1993
Transport, by train	tkm	9.56E-01	standard distances & means
Transport, by lorry	tkm	1.59E-01	standard distances & means
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
sodium sulphate	kg	1	product
hydrogen chloride	kg	0.513	co-product, stoichiometric amount
waste heat, to air	MJ	2.34E-01	calculated from electricity input
sulphate, to air	kg	1.42E-03	estimated as 0.2% of input
sodium, ions, to water	kg	1.70E-02	calculated from water emissions
chloride, to water	kg	2.63E-02	calculated from water emissions
sulphate, to water	kg	3.42E-02	calculated from water emissions

Allocation rules

Besides 1 kg of sodium sulphate, the here examined process produces in addition 0.513 kg hydrogen chloride. As both of them have prices that are quite high – here hydrogen chloride is taken as a co-product and thus an allocation has to be established. Therefore, the prices of the two substances are used – except for the input of raw material, those are allocated according to the stoichiometric mass balance in the products. The different allocation factors are summarized in Tab. 78.4.

Tab. 78.4 Allocation factors used in the ecoinvent project for the Multi-Output process “Sodium sulphate, Mannheim process, at plant (RER)”

(i) Allocation according to the price				
	Price [US\$/t]	Production [t]	Earnings [US\$]	Allocation-factor
Na ₂ SO ₄	124.30	1	124.30	75.4%
HCl	79.20	0.513	40.63	24.6%

(ii) Allocation accoring to stoichiometric masses		
	Allocationfactors	
	Na ₂ SO ₄	HCl
NaCl	39.3%	60.7%
H ₂ SO ₄	97.9%	2.1%

78.7 Sodium sulphate, production mix, at plant (Location: RER)

This dataset contains the in chapter 78.4 mentioned mix of the different production processes. Furthermore, the efforts for the by-products are not inventorized in a separate module but directly within this module here. According to the general methodology of the ecoinvent project (see Frischknecht et al. (2003)), a by-product is burden free – thus this dataset here contains only the efforts for the conditioning of these by-products. As no information are available about the detailed steps within the conditioning, only a rough estimation for the respective energy consumption, based on the energy consump-

tion in a large chemical plant (Gendorf (2000)) is taken into account within this dataset here. The resulting input data are summarized in Tab. 78.5.

Tab. 78.5 Energy and material demand for the production mix of sodium sulphate

[per kg sodium sulphate]			Remark
INPUTS			
sodium sulphate, from natural source	kg	0.60	estimated from literature
sodium sulphate, from Mannheim process	kg	0.15	estimated from literature
Electricity, medium voltage	kWh	0.333	estimation
Natural gas, burned in industrial furnace >100kW	MJ	2	estimation
OUTPUTS			
sodium sulphate, production mix	kg	1	product
waste heat, to air	MJ	1.20E+00	calculated from electricity input

78.8 Data quality considerations

The following three tables show the data quality indicators for the inventories of sodium sulphate production described above. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventories of the sodium sulphate production have a high uncertainty, because only few data of the three production processes were available. The data for the material input was assessed with assumptions esp. stoichiometric calculations. Energy data are taken from other processes (NaCl) esp. from literature (for Mannheim process), leading in the latter case to a lower uncertainty. The highest uncertainties exist for the emissions. Due to missing data these values are based mainly on assumptions and approximations. Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoichiometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecospold meta information from these datasets are listed in chapter 78.11.

Tab. 78.6 Input / Output and uncertainty for the process “sodium sulphate, from natural sources, at plant (RER)”

Explanation	Name	Location	Unit	sodium sulphate, from natural sources, at plant		uncertaintyType	standardDeviation95%	GeneralComment	
				RER	0				
				kg	kg				
Resources Input from Technosphere	sodium sulphate, various forms, in ground	UCTE	kg	1.05E+00	1	1.21	(4,na,na,na,na,na); assumption of yield = 95%		
	electricity, medium voltage, production UCTE, at grid		kWh	1.70E-01	1	2.1	(1,5,1,3,5,5); estimated, based on NaCl production data		
	light fuel oil, burned in industrial furnace 1MW, non-modulating		RER	1.91E-01	1	2.1	(1,5,1,3,5,5); estimated, based on NaCl production data		
	diesel, burned in building machine		GLO	4.28E-03	1	2.1	(1,5,1,3,5,5); estimated, based on NaCl production data		
	chemical plant, organics		RER	2.00E-10	1	3.77	(4,5,1,3,5,5); estimation		
	disposal, inert waste, 5% water, to inert material landfill		CH	3.00E-02	1	2.1	(1,5,1,3,5,5); estimated, based on NaCl production data		
Output Air emission	sodium sulphate, from natural sources, at plant		RER	kg	1				
	Heat, waste			MJ	6.12E-01	1	2.1	(1,5,1,3,5,5); calculated from electricity input	
	Sulfate			kg	2.58E-02	1	2.11	(5,5,na,na,4,5); assuming 2.5% of input material as emission	

Tab. 78.7 Input / Output and uncertainty for the process “sodium sulphate, Mannheim process, at plant (RER)”

Explanation	Name	Location	Unit	sodium sulphate production, Mannheim process, at plant		UncertaintyType standardDeviation95%	GeneralComment		sodium sulphate, from Mannheim process, at plant	hydrochloric acid, from Mannheim process, at plant	
							RER 0 kg	RER 0 kg			
				Location							
				InfrastructureProcess							
				Unit							
Resources	Water, cooling, unspecified; natural origin		m3	2.60E-02	1	1.46	(4.5,1,5,3,5); information from Ullmann's Encyclopedia	75.4	24.6		
Input from Technosphere	Water, unspecified natural origin		m3	1.40E-03	1	1.46	(4.5,1,5,3,5); information from Ullmann's Encyclopedia	75.4	24.6		
	sodium chloride, powder, at plant	RER	kg	8.66E-01	1	1.21	(4.na,na,na,na,na); stoichiometric calc., yield 99.8%-90%	39.3	60.7		
	sulphuric acid, liquid, at plant	RER	kg	7.27E-01	1	1.21	(4.na,na,na,na,na); stoichiometric calc., yield 99.8%-90%	97.9	2.1		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	6.50E-02	1	1.46	(4.5,1,5,3,5); information from Ullmann's Encyclopedia	75.4	24.6		
	natural gas, burned in industrial furnace >100kW	RER	MJ	1.80E+00	1	1.46	(4.5,1,5,3,5); information from Ullmann's Encyclopedia	75.4	24.6		
	heavy fuel oil, burned in industrial furnace 1MW, non-modulating	RER	MJ	1.80E+00	1	1.46	(4.5,1,5,3,5); information from Ullmann's Encyclopedia	75.4	24.6		
	transport, freight, rail	RER	tkm	9.56E-01	1	2.09	(4.5,na,na,na,na); standard distances	75.4	24.6		
	transport, lorry 32t	RER	tkm	1.59E-01	1	2.09	(4.5,na,na,na,na); standard distances	75.4	24.6		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4.5,1,5,4); estimation	75.4	24.6		
Output	sodium sulphate, from Mannheim process, at plant	RER	kg	1				100	0		
	hydrochloric acid, from Mannheim process, at plant	RER	kg	0.513				0	100		
Air emission	Heat, waste		MJ	2.34E-01	1	1.46	(4.5,1,5,3,5); calculated from electricity input	75.4	24.6		
Water emission	Sulfate		kg	1.42E-03	1	1.88	(5.5,na,na,na,5); assumption, 0.2% of input = air emission	75.4	24.6		
	Sulfate		kg	3.42E-02	1	2.11	(5.5,na,na,4.5); calculated from mass bilance	75.4	24.6		
	Sodium, ion		kg	1.70E-02	1	2.11	(5.5,na,na,4.5); calculated from mass bilance	75.4	24.6		
	Chloride		kg	2.63E-02	1	2.11	(5.5,na,na,4.5); calculated from mass bilance	75.4	24.6		

Tab. 78.8 Input / Output and uncertainty for the process “sodium sulphate, powder, production mix, at plant (RER)”

Explanation	Name	Location	Unit	sodium sulphate, powder, production mix, at plant		UncertaintyType standardDeviation95%	GeneralComment		sodium sulphate, from Mannheim process, at plant	hydrochloric acid, from Mannheim process, at plant	
							RER 0 kg	RER 0 kg			
				Location							
				InfrastructureProcess							
				Unit							
Input from Technosphere	sodium sulphate, from natural sources, at plant	RER	kg	6.00E-01	1	1.24	(3.1,2,2,1,5); information from US market survey				
	sodium sulphate, from Mannheim process, at plant	RER	kg	1.50E-01	1	1.24	(3.1,2,2,1,5); information from US market survey				
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5.5,1,1,4,5); estimated with data from 1 large chemical plant				
	natural gas, burned in industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5.5,1,1,4,5); estimated with data from 1 large chemical plant				
Output	sodium sulphate, powder, production mix, at plant	RER	kg	1							
Air emission	Heat, waste		MJ	1.20E+00	1	1.88	(5.5,1,1,4,5); calculated from electricity input				

78.9 Cumulative results and interpretation

Results of the cumulative inventory for these substances can be downloaded from the database.

78.10 Conclusions

The different inventories for sodium sulphate are based on general literature sources (US Minerals Yearbook resp. Ullmann), estimations and assumptions. The different unit process raw data are meant to be used as background information if the respective form of sodium sulphate is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of these substances with other, alternative products.

78.11 EcoSpold Meta Information

ReferenceFunction	Name	sodium sulphate, from natural sources, at plant	sodium sulphate production, Mannheim process, at plant	sodium sulphate, powder, production mix, at plant
Geography	Location	RER	RER	RER
ReferenceFunction	InfrastructureProcess	0	0	0
ReferenceFunction	Unit	kg	kg	kg
ReferenceFunction	IncludedProcesses	Resource amount from estimated yield, energy consumption from a similar process (NaCl exploitation). Infrastructure and emissions, waste estimated.	Raw materials and chemicals used for production, transport of materials to manufacturing plant, emissions to air and water from production, estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.	Mixture of three different ways for the production of sodium sulphate: from natural resources, as by-product out of other processes, as main product from chemical processes. Energy amount for conditioning of by-product sodium sulphate included here.
ReferenceFunction	Amount	1	1	1
ReferenceFunction	LocalName	Natriumsulfat, aus natürlichen Vorkommen, ab Werk	Natriumsulfatproduktion, Mannheim-Prozess, ab Werk	Natriumsulfat, Pulver, ab Werk
ReferenceFunction	Synonyms			
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of exploitation of naturally occurring sodium sulphate. Very large uncertainty of the process data, as only a mixture of different materials is included.	The multioutput process "sodium sulphate production, Mannheim process, at plant" delivers the co-products sodium sulphate, Mannheim process, at plant" and hydrochloric acid, Mannheim process, at plant". An allocation to the two products is done by using the price rsp. for the raw materials stoichiometric mass. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.	The functional unit represent 1 kg of sodium sulphate powder. Very large uncertainty of the process data due to the weak data on the process.
ReferenceFunction	CASNumber			
TimePeriod	StartDate	2000	2000	2000
TimePeriod	EndDate	2000	2000	2000
TimePeriod	DataValidForEntirePeriod	1	1	1
TimePeriod	OtherPeriodText			
Geography	Text	Data used has no specific geographical origin (see included processes). Data are used as European average data.	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.	Mix of different production ways based on information about global production. Data are used as European average data.
Technology	Text	mixture of brine evaporation and further treatment - based on data of NaCl production	Production of sodium sulphate and HCl by the so-called Mannheim process	data represent a mixture of three possible production ways. Natural resources by evaporation & further treatment, by product out of chemical industry, main product from Mannheim process (NaCl & H2SO4).
Representativeness	Percent			
Representativeness	ProductionVolume	unknown	unknown	worldwide production 5.5 Mt in 1997
Representativeness	SamplingProcedure	estimations out of similar processes	literature	literature and estimations out of similar processes
Representativeness	Extrapolations	see technology and geography	see technology and geography	see technology
Representativeness	UncertaintyAdjustments	none	none	none

78.12 References

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79 Soya oil

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Last Changes:

2004

79.1 Introduction

Soya oil, also called soybean oil, (CAS Nr 8001-22-7) is light yellow coloured and has a mild taste. It is rich in polyunsaturated fatty acids and contains no cholesterol. Because it is manufactured from soybeans it represents a good source of calcium, iron, zinc, phosphate, magnesium, B vitamins and folate. Tab. 79.1 shows the fatty acid profile of soya oil.

Tab. 79.1 Fatty acid profile of soya oil. (Based on ASA 2003)

Fatty Acid	Composition (%)
SATURATED	
C12 (lauric acid)	tr ¹
C14 (myristic acid)	tr
C16 (palmitic acid)	11.0
C18 (stearic acid)	4.1
C20 (arachidic acid)	tr
UNSATURATED	
16:1 (palmitoleic acid)	tr
18:1 (oleic acid)	22.0
18:2 (linoleic acid)	54.0
18:3 (linolenic acid)	7.5

¹ tr: traces.

Soya scrap or soybean meal is also generated in the manufacturing process of soya oil. It consists basically on the spent press-cake. The following description of reserves and resources as well as production technology and use of soya oil and soja scrap are summarised from Berk (1992), Rossel (2001), and ASA (2003).

79.2 Reserves and Resources

The resources available as well as the reserves are the same as for the agricultural production of soya beans, described in the corresponding chapter.

Soya oil is nowadays the most important edible oil in the world market, with 28% share of the total. The soya scrap is also an appreciated product because of its high protein content. It has such an economic relevance in the agricultural sector that it is considered that the market of soya scrap actually drives the one from oil.

Throughout the 1990's, the world supply and demand situation for soya oil showed a continuous progression of new record highs. World production in 1999/2000 was 24 Mio Tons. The U.S., the world's largest soya oil producer, generally accounts for about a third of total production. Brazil, the world's second largest producer, typically accounts for about 16 percent of the world total. World usage of soya oil in 1999/00 was 23.9 Mio Tons. The U.S. is the largest consumer with China a distant second.

79.3 Production Technologies and Use

79.3.1 Production technologies for the production of soya oil and soya scrap

The manufacturing of soya oil can be accomplished by physical or chemical means, using pressing- or solvents extraction- techniques. A combination of both may also be used.

1.3.1.1 The expeller (screw press) process

Continuous pressing by means of an expeller, also known as screw press, is a widely applied process for the extraction of oil from oilseeds and nuts. Nevertheless, in the soya oil industry, this process is used mainly in small plants because of its low oil recovery yield. Another disadvantage from this process is that it produces a soya scrap of low quality and stability. The expeller consists of a screw rotating inside a cylindrical cage. The material to be pressed is fed between the screw and the barrel and propelled by the rotating screw in a direction parallel to the axis. Before entering the expeller, the beans must be cleaned, dehulled (optional), flaked, cooked and dried.

1.3.1.2 The solvent extraction process

Fig. 79.1 shows the main steps in the manufacturing process of soya oil and soya scrap by means of solvent extraction. The solvent extraction is the most relevant process currently in use in Western countries for the manufacturing of soya oil.

Preparation of the beans

First, the soya beans have to be prepared. They are cracked, conditioned with heat to get the necessary plasticity and finally flattened in the flaker. If the beans have been dried before entering this conditioning process, they became dehulled in the cracking step. It must be noticed that dehulling is necessary only if the process is designed to obtain certain kind of scrap. As alternatives to these conventional oil-mill operations, improved processes have been suggested for individual steps or for the whole seed preparation line. The so-called “hot dehulling system” makes use of a shock treatment to loosen the hull. The Alcon process is, essentially, an agglomeration process, whereby the flakes are humidified and fused into more compact, porous granules.

In some cases, a **pre-pressing** step is performed on the beans after the preparation step described above and before entering extraction.

Extraction

The extraction of oil from oilseeds by means of non-polar solvents is, basically, a process of solid-liquid extraction. The oil is extracted from the flakes by means of an organic solvent (hexane) and the micelle is built. This micelle contains approximately 70-75% oil and 25-39% hexane. The solvent is afterwards recovered.

Crude oil refining

Once the crude oil is obtained, it must be further refined. **Degumming** is the removal of the phospholipids from the oil. This is necessary in order to prevent the separation and settling of gums, to reduce losses in the subsequent phases of refining and to avoid excessive darkening of the oil during the deodorisation step. At the degumming step oil free soybean phospholipids are generated. These by-products are known as soybean **lecithine** and sold under different trade names.

After degumming the crude oil must undergo further refining. In the **deacidification step** free fatty acids are removed. The most common process for this purpose is the chemical or caustic refining process, by which fatty acids are neutralized with alkali (sodium hydroxide or sodium carbonate) to form salts (soaps) soluble in water. This treatment with caustic solutions also removes residues of phospholipids not removed by degumming and results in some degree of bleaching due to the destruction of some of the pigments or their adsorption by the heavy phase. The resulting aqueous soap solution, known as "soap stock" is removed from the neutralized oil by centrifugation. The oil is thoroughly mixed with hot water to remove traces of soap (washing), then centrifuged again and dried by heating under vacuum, in preparation for the next step, bleaching. Soap stock can be used for making soap or it can be converted back to fatty acids by treating with a strong mineral acid. The crude mixture of fatty acids obtained, known also as acidified soap stock can be used as a caloric component in animal feed or for the manufacture of distilled fatty acids. In the physical removal, less commonly applied, free fatty acids are removed by steam distillation under high vacuum, simultaneously achieving deodorisation. (Oil for physical refining must be degummed more thoroughly than in the case of alkali refining process.)

The next step of refining is **bleaching**. Its purpose is to remove the carotenoid pigments and the green chlorophyll of the oil. The extent of bleaching depends on market requirements. This process step is carried out by treating the oil with solid adsorbents such as Fuller's earth or activated carbon or both. The pigments and some other impurities are adsorbed on the solid surface and removed by filtration. In order to prevent oxidation, the process is carried out under vacuum. Continuous "in flow" bleaching process are available.

The last refining operation is **deodorisation**. It consists in the removal of odorous substances by steam distillation under high vacuum and at temperatures in the range of 250°C. Typically, the deodoriser is a vertical cylindrical vessel with internal baffles and other devices to ensure exposure of a large surface area of oil and intimate contact between the oil and steam. Afterwards, the oil is cooled and citric acid is added to chelate metal ions that may catalyse peroxide formation. All the substances removed in the deodorisation may be recovered from the deodoriser condensate stream.

Production of soya scrap for animal feedstuff

Soya cake and soya meal are produced in the same manufacturing process with soya oil. Although these terms and soya scrap are often used interchangeably, meal refers to the product of solvent extraction while cake is the product of expeller pressing of soya beans. For this study, soya scrap is used as synonym for soya meal.

The fat-free scrap originated in the oil process still contains approx 30% hexane, which has to be extracted in the desolventiser-toaster. In this step the protein in the bean is also heated and thus its nutrition value increases (trypsin-inhibitors and other substances are deactivated).

The different types of soya meals are characterised mainly by their protein content and the extent of heat treatment applied in their production to inactivate anti-nutritional factors. The extent of heat treatment or toasting applied depends on the intended final application of the soya scrap. Thus, a meal containing about 44% protein is obtained when the soya beans are extracted without dehulling, or if the hulls are added back after extraction. Meals produced from dehulled beans contain approximately 50% protein.

Other scrap-products obtained in the soya oil manufacturing process

Other products beside scrap for animal feedstuff can be obtained from the scrap (meal) fraction. These have specific quality and sanitary standards to be met and therefore, also specific operation requirements. Some of them are: deffated soybean flours and grits for human consumption, soybean protein concentrates (70% protein), soybean protein isolates and extrusion-textured soybean protein.

Generation of by-products

Lecithin is the principal by-product generated in the oil manufacturing process. It usually enters the soya scrap manufacturing process but it is sometimes also sold as a product. Lecithine is a natural emulsifier and lubricant and therefore it has many uses from pharmaceuticals to protective coatings.

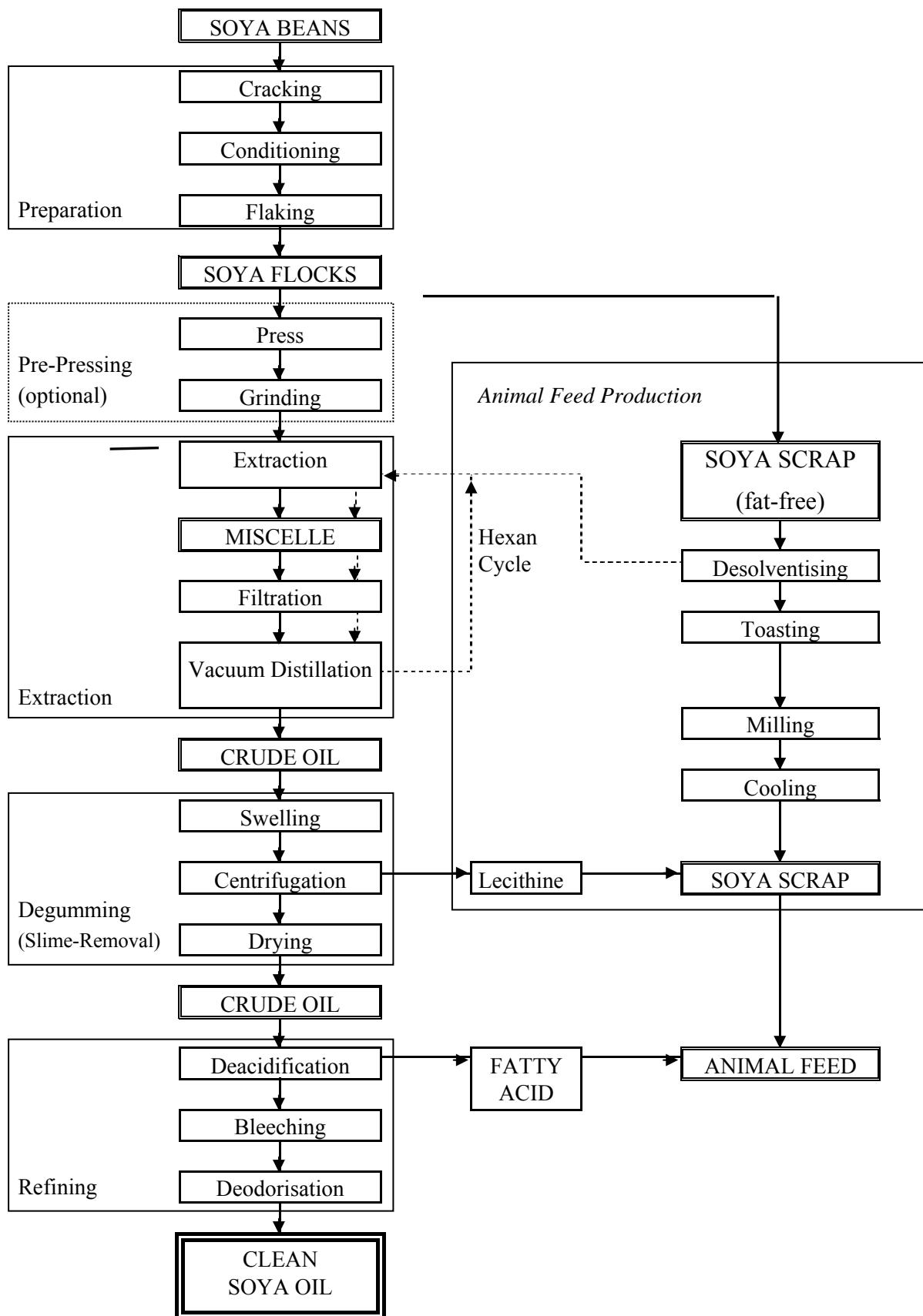
Auxiliary processes before/after soya oil production

In some cases the soya beans entering the manufacturing plant have to be **dried** before entering the preparation process described above and illustrated in Fig. 79.1. This is necessary if the soya beans are to be dehulled before extraction and they come to the manufacturing plant with a moisture content above 10%. After cooling, the soya beans are stored in bins for 2 to 5 days in order to allow for moisture equilibration.

Before entering the extraction process, the beans must also be **cleaned** to remove metals, stones, sand, dust and other foreign materials. For this purpose different devices are used, for example magnetic separators and seed cleaners.

The final product soya oil has to be adequately handled in order to avoid flavor deterioration. For this purpose, the oil is bottled under conditions of minimal exposure to oxygen and to light, i.e. bottling under nitrogen and using opaque containers and dark glass bottles. Another method for **flavor stabilisation** is the reduction of the linoleic content by selective hydrogenation, followed by chilling (wintering) to remove the high melting point saturated fatty acids formed. The partially hydrogenated-winterised soya oil is perfectly suitable as an all-purpose oil. The crystalline fraction separated after chilling is known as "soybean stearin" and is used in different solidified fats. More complete hydrogenation of soya oil is the basis for the manufacture of shortenings, margarines and tailor-made fats used by various food industries.

Fig. 79.1 Production of soya oil and soya scrap with solvent extraction. (Taken from Reusser 1994, Fig. 3.1)



79.3.2 Use

Despite its relatively low fat content, soya oil is very valuable because of its protein and unsaturated fatty acids content. Soya oil is one of the most used basic products for the manufacturing of margarine, edible- and cooking oils and fats. Additionally, soya oil has many industrial applications for example, in the manufacturing of anti-corrosion agents, fuels, disinfectants, pesticides and fungicides, electric insulation, and it is also used in the painting industry.

By far the largest portion of soya scrap is used as a protein source for animal feeding. It is also used as a protein source for human consumption. The importance of soya scrap in the market is very high, so that soya oil is sometimes considered as its by-product.

79.4 System characterization

This report corresponds to the module “**soya oil, production**” in ecoinvent database. It is a multioutput process with two outputs: **1 kg soya oil, at plant, in Europe**, and **4.6 kg soya scrap, at plant, in Europe**.

It is considered that production bases on 94% imported soya beans from overseas and 6% locally produced soya beans. This, according Reusser (1994), one of the data sources used in this study.

For this study the production of soya oil with the **solvent extraction process** is considered as it is described in Fig. 79.1. **All data in the present report are referred to 1 kg soya oil 100% and 4.6 kg soya scrap.**

The system includes the process with the consumption of raw materials, auxiliaries, energy, infrastructure and land use, as well as the generation of solid wastes and emissions into air and water. It also includes transportation of raw materials and auxiliaries.

In this study, soya oil and soya scrap are considered co-products, since both are of similar economic relevance, as already mentioned. An allocation is done between both products, corresponding 28 % to oil and 72 % to scrap. (See 1.6 Allocation procedures). In this study, the term soya scrap refers to the soya meal with 44% protein. The generation of by-products, like lecithin or other, is not included. Due to the lack of information, no values for solid wastes can be presented and therefore, the generation and transportation of wastes is not included.

For the study, transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Bottling, packaging, storage and transportation of the final products soya oil and soya scrap are also not included. For this study, the production of soya oil is considered to base on dried soya beans and therefore the drying of the beans is not included here.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers.

It is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

79.5 Soya oil production process

79.5.1 Data sources

Main data sources for this study are Reusser (1994) and Cederberg (1998) – von Däniken *et al.* (1995) is taken into account for plausibility checks and comparison reasons.

Reusser (1994) is a Swiss study on the ecobalance of the production of soya oil. It bases on literature data as well as on confidential data provided by manufacturing plants. No further information is avail-

able on the mentioned manufacturing companies (production capacity, technology used, etc). There is also no information on the data themselves. Therefore, it is difficult so assess the representativeness of these data.

Cederberg (1998) is a Swedish Life Cycle Assessment of Milk Production that presents values for soya bean processing. For oil and scrap production, this source bases on information from Denofa, the single oil and fat producer in Norway, and from Krupp Extraktionstechnik GmbH, a machinery supplier for the extraction industry.

von Däniken *et al.* (1995) is a study from the Swiss Agency for the Environment, Forests and Landscape (BUWAL). This study bases on confidential information provided in the early nineties by a European manufacturing company and on estimations and calculations of the authors. No further information is available on the mentioned manufacturing company (production capacity, technology used, etc) or on the data themselves. Therefore, it is difficult so assess the representativeness of the data presented in this source.

79.5.2 Raw materials and auxiliaries

von Däniken *et al.* (1995) indicates a consumption of 5 kg soya beans per kg oil produced. Reusser (1994) mentions a value of 5.6 kg soya beans per kg oil produced. For this study, the value from Reusser (1994) is taken because this source seems to have a better support of data. To choose the highest value is also in concordance with the conservative criterion used in this study.

Cederberg (1998) states an input of 4.00 E-04 kg hexane per kg soya bean used, what means 2.24 E-03 kg hexane per kg soya oil produced (considering an input of 5.6 kg bean per kg oil manufactured). For ecoinvent database, the module correponding to pentane is taken since there is no module available for the production of hexane. This should not affect the quality of the present study because the manufacturing processes of both chemicals are similar.

Further information about the amounts of auxiliaries used in the manufacturing process is not available.

79.5.3 Energy and transportation

Energy

In von Däniken *et al.* (1995), the values regarding energy base on information provided by a European company. This information consists on consumption of electricity and thermic process energy. Basing on the latter (6.38 MJ per kg oil), the authors calculate the consumption of different energy carriers.

Reusser (1994) also presents values for consumption of electricity and steam. Basing on the latter (3.86 MJ per kg oil), he calculates the consumption of natural gas and fuel oil.

Cederberg (1998), again, gives values for consumption of electricity and steam. This source mentions an imput of 2.80 E-01 to 3.16 E-01 kg steam per kg oil produced. The first value corresponds to a machinery supplier and represents a high technology level according the source; the second corresponds to a Norway oil manufacturing company. For this study, only the second value is considered since it seems more representative for the average European soya oil industry.

The information regarding consumption of energy in the different sources consulted is shown in Tab. 79.2.

Tab. 79.2 Energy consumption for the production of soya oil.

Input. kg⁻¹ soya oil	von Däniken et al. (1995)	Reusser (1994)	Cederberg (1998)	This study
electricity kWh	2.70 E-01 ¹	1.21 E-01	2.58 E-01	2.58 E-01
hardcoal kg	6.77 E-02			
heavy fuel oil kg	2.85 E-02			
light fuel oil kg	6.20 E-03	2.90 E-02		2.90 E-02
natural gas m ³	8.10 E-02	6.30 E-02		6.30 E-02

¹: value provided by a European company.

The electricity consumption reported by Reusser (1994) is approximately the half of the numbers from von Däniken *et al.* (1995) and Cederberg (1998). This value in Reusser (1994) seems to low also for experts from the agricultural sector⁶ and therefore, is not taken into consideration. For this study, the value from Cederberg (1998) is taken.

In regard to consumption of thermal energy, Reusser (1994) and Cederberg (1998) present similar numbers. The higher numbers in Reusser (1994), can be explained by the fact that this source bases not only on information from manufacturing plants (that could be less efficient than the Norway one), but also on literature that consider an average scenario. The numbers of Reusser 1994 are used for this study. von Däniken *et al.* (1995) presents a value that is twice the numbers in the other sources and is not taken into consideration, also due to the fact that the data originated only at one manufacturing plant. For both fuels, the respective „heating“ modules are used (see remarks for emissions to air).

Transportation

According to Reusser (1994), transportation of the soya beans plays an important role in the soya oil industry. In the mentioned source, two scenarios are considered and transportation amounts are estimated. One refers to the hypothetically production of soya oil in Switzerland based on Swiss soya beans. The second scenario, according the real situation of the industry, considers the production based on imported soyabean from overseas. In this study, the numbers for this second scenario are used. This due to the fact that also the European soya oil production is based on imported beans.

von Däniken *et al.* (1995) do not consider transportation in their survey.

No information is available in the examined data sources for transportation of auxiliaries or solid wastes. Therefore, for the auxiliaries, standard distances as defined in Frischknecht *et al.* (2004) were used: 100 km by lorry 32t and 600 km by train. Transport amounts for solid wastes cannot be made because there are no values even for generation of wastes.

Tab. 79.3 summarises the total transport amounts for the production of 1 kg soya oil based on beans from overseas.

⁶ T. Nemecek (2003). Oeko-Controlling Oekobilanzen. Forschungsanstalt für Agrarekologie und Landbau (FAL). Personal communication on 25.03.2003

Tab. 79.3 Total transport amounts and means for the production of soya oil based on imported soya beans from overseas.

(tkm. kg ⁻¹ soya oil)	lorry	train	overseas ship	Rhein ship
raw material	8.15 E+00	1.96 E+00	6.74 E+01	4.50 E+00
auxiliaries	2.24 E-05	1.34 E-04	0	0
waste to disposal sites	nd	nd	nd	nd
Total transports	8.15 E+00	1.96 E+00	67.39 E+00	4.50 E+00

nd: no data available

Rhein ship is reported in ecoinvent database as “transport barge“.

79.5.4 Infrastructure and land use

There is no information available about infrastructure and land-use of soya oil plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see part I of this report. Thus, for this study, the estimated value is 4.00 E-10 unit. kg⁻¹ soya oil.

79.5.5 Production of soya-scrap

Reusser (1994) mentions a generation of 4.6 kg soya scrap per kg soya oil produced. Rossel (2001) indicates a production of 4.5 kg soya scrap with 44% of raw protein. von Däniken *et al.* (1995) do not consider the manufacturing of this co-product. The value from Reusser is used in this study.

79.5.6 Emissions to air and water

von Däniken *et al.* (1995) present values for specific process emissions to air and also numbers for emissions to water. Cederberg (1998) gives values for the emission of hexane into air.

Emissions to air

The different used sources contain only process emissions but no combustion emissions although the production chain uses fossil fuels. Thus, the only possibility for an adequate integration of combustion emissions is to use the respective heating modules for the different fuels – modules that contain the correct combustion emissions to air.

For the process emissions von Däniken *et al.* (1995) mentions the emission of 3.00 E-04 kg HCl (per kg soya oil) arised by the manufacturing process. Reusser (1994) mentions a hexan emission into air of 5.00 E-04 to 1.00 E-03 kg per kg manufactured oil. Cederberg (1998) gives for the emission of hexane to air a value of 2.00 E-04 kg hexane per kg soya bean used, what means 1.12 E-04 kg hexane per kg oil produced. For this study, an average of the values presented by Reusser (1994) is used (7.50 E-04 kg hexane per kg oil manufacture). The mentioned value is taken following a conservative criterion.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. This waste heat is reported in Mega Joules (MJ). Therefore, a conversion from kWh to MJ is necessary. According to Frischknecht *et al.* (2004) and considering the electricity input of 2.58 E-01 kWh per kg soya oil, the value of waste heat due to electricity consumption for this study is 9.29 E-01 MJ per kg soya oil manufactured.

Emissions to water

In the manufacturing of soya oil, there are three principal sources of waste waters:

- process water, that is contaminated with oil to different degrees and is separately collected in each step of the process
- cooling water, that in normal operating conditions should be uncontaminated.
- rain water, also uncontaminated excepting if it comes into contact with dirty surfaces.

The contaminated waste water is cleaned in a gravitation-separation system. Von Däniken *et al.* (1995) presents values for emission to water of dissolved solids and COD. The sources consulted do not present any further numbers for emissions into water.

All available information about emissions to air and water is summarised in Tab. 79.4.

Tab. 79.4 Emissions to air and water of the production of soya oil.

(kg.kg ⁻¹ 100% soya oil)	von Däniken <i>et al.</i> (1995)	Reusser (1994)	This study
<i>Emission to air</i>			
Waste heat			9.29 E-01
Hexane		7.50 E-04	7.50 E-04
Hydrogen chloride	3.00 E-04		3.00 E-04
<i>Emission to water</i>			
Dissolved solids	2.00 E-05		2.00 E-05
COD	3.00 E-03		3.00 E-03

79.5.7 Wastes

Rossel (2001) mentions the generation of used filter-cake. This cake consists of bleaching earth and filter-auxiliary. This residue is inert and has an oil content of 25 to 100%. It is either reused as processing aid for soja scrap or it is sent to landfill. The manipulation of this material has to be done carefully because of the explosion risk. Spent hydrogenation-catalysts can be recycled. However, when the metal content in the spent catalysts is too low, the dealers are no interested in them. This applies mostly to nickel content. Another solid waste to be mentioned is the sludge from wastewater treatment.

von Däniken *et al.* (1995) indicates that there are no solid wastes arised by the production of soya oil. In the other consulted sources no numbers for solid waste are either available.

For this study, solid waste is reported as “disposal, municipal solid waste, 22.9 %water, to sanitary landfill“, due to lack of further information about the composition of the wastes mentioned. This is considered the most appropriate among the different modules available in the database.

79.6 Allocation procedures

For this study, the allocation between the co-products soya oil and soya scrap is accomplished on price. This criterion is chosen basing on the opinion of experts from the agricultural sector⁷ and in concordance to Cederberg (1998). The marketprices of soya oil is 0.515 U\$D/kg and the one of soya scrap, 0.292 U\$D/kg (Cederberg (1998), Table 4.7).

It must also be taken into account that in the manufacturing process basing on 5.6 kg soya beans, 1 kg soya oil and 4.6 kg soya scrap are generated, what means 0.515 U\$D for oil and 1.343 U\$D for scrap. That means 28% corresponding to oil and 72% to scrap.

Thus, in general, 28% are allocated to soya oil and 72% to soya scrap. The consumption of pentane in the extraction step and also the emission of hexane into air are allocated only to oil, since the hexane is used to increase the oil extraction. In order to fulfil the mass balance, the input amount of soya beans as well as all transport efforts (those refer to the transport of the soya beans to the oil extraction mill) are allocated according to mass – i.e. 17.9% to oil, 82.1% to soya scrap.

79.7 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The main concern in regard to the data sources is that they base on little direct information from manufacturing plants. The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht *et al.* (2003) (transport) resp. the very general module of an organic chemical plant are used. This lack of representativeness is reflected in the uncertainty scores.

Tab. 79.5 summarises the input and output data as well as the uncertainties used for the production of soya oil and soya scrap. All of these are multi-output models. Allocation factors are given in the last two columns. The values are given for the production of 1 kg soya oil and 4.6 kg soya scrap.

Tab. 79.5 Input- / Output-data for the soya oil production (all values are referred to the production of 1 kg soya oil and 4.6 kg soya scrap) as well as the allocation factors of the respective input- / output-data

Explanation	Name	Location	Unit	soya oil, production			GeneralComment	soya oil, at plant	soya scrap, at plant
				RER	0	kg			
				Uncertainty	Type	StandardDeviations%			
Input from Technosphere	pentane, at plant	RER	kg	2.24E-3	1	1.32	(3.5,1,3,1,5); Data from survey in literature (Cederberg 1998)	100.00	0.00
	soy beans IP, at farm	CH	kg	5.60E+0	1	1.34	(3.5,3,3,1,5); Data from survey in literature (Reusser 1994)	17.90	82.10
	natural gas, burned in industrial furnace >100kW	RER	MJ	2.29E+0	1	1.34	(3.5,3,3,1,5); Data from survey in literature (Reusser 1994)	28.00	72.00
	light fuel oil, burned in industrial furnace 1MW, non-modulating	RER	MJ	1.24E+0	1	1.34	(3.5,3,3,1,5); Data from survey in literature (Reusser 1994)	28.00	72.00
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	2.58E-1	1	1.32	(3.5,1,3,1,5); Data from survey in literature (Cederberg 1998)	28.00	72.00
	transport, lorry 32t	RER	tkm	8.15E+0	1	2.12	(3.5,3,3,1,5); Data from survey in literature (Reusser 1994)	17.90	82.10
	transport, freight, rail	RER	tkm	1.96E+0	1	2.12	(3.5,3,3,1,5); Data from survey in literature (Reusser 1994)	17.90	82.10
	transport, transoceanic freight ship	OCE	tkm	6.74E+1	1	2.12	(3.5,3,3,1,5); Data from survey in literature (Reusser 1994)	17.90	82.10
	transport, barge	RER	tkm	4.50E+0	1	2.12	(3.5,3,3,1,5); Data from survey in literature (Reusser 1994)	17.90	82.10
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4.1,5,3,5,4); Estimation	28.00	72.00
Output	soya oil, at plant	RER	kg	1.00E+0				100.00	0.00
	soya scrap, at plant	RER	kg	4.60E+0				0.00	100.00
air emission	Heat, waste	MJ		9.29E-1	1	1.32	(3.5,1,3,1,5); calculated from electricity input	28.00	72.00
	Hydrogen chloride	kg		3.00E-4	1	1.65	(3.5,3,3,1,5); Data from survey in literature (van Däniken et al. 1995)	28.00	72.00
	Hexane	kg		7.50E-4	1	2.12	(3.5,3,3,1,5); Data from survey in literature (Reusser 1994)	100.00	0.00
water emission	Solved solids	kg		2.00E-5	1	1.65	(3.5,3,3,1,5); Data from survey in literature (van Däniken et al. 1995)	28.00	72.00
	COD, Chemical Oxygen Demand	kg		3.00E-3	1	1.65	(3.5,3,3,1,5); Data from survey in literature (van Däniken et al. 1995)	28.00	72.00

⁷ T. Nemecek (2003). Oeko-Controlling Oekobilanzen. Forschungsanstalt für Agrarekologie und Landbau (FAL). Personal communication on 25.03.2003.

79.8 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

79.9 Conclusions

An average European dataset for the production of soya oil for the year 2000 is established. The dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on a report covering the European industry, based on statistics from the first half of the 1990s. The data are thus of a reasonable quality and can be used in quite a broad context.

79.10 References

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79.11 EcoSpold Meta Information

ReferenceFunction	Name	soya oil, production
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	The inventory includes the conditioning (but not the drying) of the beans previous extraction. It also includes the production of soya scrap.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Sojaöl, Herstellung
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	Manufacturing process starting with dry soja beans (basically imported from overseas) is considered, plus consumption of auxiliaries, energy, infrastructure and land use, as well as generation of emissions into air and water. Transport of the raw materials and auxiliaries is also included. The generation of the co-product soya scrap is considered. 28% of the inputs and outputs are allocated to soya oil and 72% to soya scrap. (basing on price) Generation and transportation of solid wastes are not included due to the lack of data. Transport and storage of the final products are not included. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Inventory refers to 1 kg soya oil. The module "pentane" is used to report the consumption of hexane, since the latter is not available in ecoinvent database. Main literature sources are Reusser 1994, Cederberg 1998 and von Däniken et al. 1995.
ReferenceFunction	CASNumber	8001-22-7
TimePeriod	StartDate	1998-12
TimePeriod	EndDate	1998-12
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	Literature base on data mostly from the 1990s.
Geography	Text	values from literature, some values provided by European manufacturing companies whose representativeness for the European soya oil industry is unknown
Technology	Text	unknown
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see OtherPeriodText
Representativeness	Extrapolations	Infrastructure: proxy module used (chemical plant, organics)
Representativeness	UncertaintyAdjustments	none

80 Sulfur dioxide

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80.1 Introduction

This chapter describes the production of liquid sulfur dioxide (SO_2). This chemical is used primarily in the pulp and paper industry.

Synonyms for sulfur dioxide: sulphurous acid anhydride, sulfurous oxide

80.2 Reserves and resources of liquid sulfur dioxide

Liquid sulfur dioxide is an inorganic chemical compound. It is produced from a variety of sources, including sulfur dioxide present in flue gases or hydrogen sulfide present in natural gas.

80.3 Characterisation of liquid sulfur dioxide

Liquid SO_2 is a colorless liquid kept under pressure. It has a strong pungent odor. Liquid SO_2 has a boiling point of -10°C and a freezing point of -75.5°C . It is nonflammable. It will react with water to form sulphuric acid. Liquid SO_2 can cause frostbite and skin burns. Vapors are extremely irritating to throat and mucous membranes and upper respiratory tract. SO_2 reacts violently with peroxides, chromates and chlorates. (Data stem from Material Safety Data Sheets of various producers)

80.4 Production and use of liquid sulfur dioxide

US demand: 2000: 438 thousand tonnes; 0% growth projected through 2003 according to Chemical Profiles published in the Chemical Market Reporter. No figures were readily available for Europe. However, a major German producer generated 70'000 tonnes of SO_2 from recycling sulfur-containing wastes in previous years according to (UBA 1/2000).

Tab. 80.1 Uses of liquid sulfur dioxide (Chemical Profiles, 2000)

Chemicals*	40%
Pulp and paper	23%
Food & agriculture **	14%
metal and ore refining	6%
Oil recovery and refining	4%
miscellaneous	4%

* sodium hydrosulfite 20%, others 20%

** primarily corn

Sodium hydrosulfite is mostly used for wood pulp bleaching.

80.5 System characterization

There are widely varying processes for the production of liquid SO_2 .

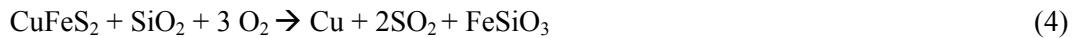
80.5.1 SO₂ from the combustion of sulfur

Sulfur, obtained either from natural deposits or from sulfur recovery (see below) is combusted in a chamber. The SO₂ gas content is generally up to 18% by volume. This process is exothermic.



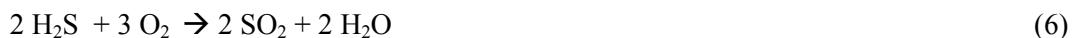
80.5.2 SO₂ from metal sulfide roasting (German BAT Notes)

Ore concentrates are roasted in smelters. The SO₂-content of the gases is 5-10 %. Zink sulfide (2) or lead sulfide (3) can be roasted on a fluidized bed. Pyrometallurgical copper extraction (4) is based on the decomposition of copper – iron minerals into copper sulfides, followed by oxidation. Pyrite (5) can be roasted in various types of furnaces. The SO₂-content of the gases is 6-14 %.



80.5.3 SO₂ by means of sulfur recovery (Claus process)

Sulfur recovery converts hydrogen sulfide gas (H₂S) to elemental sulfur and SO₂. H₂S is a by-product of processing natural gas and is also contained in the off-gases of oil refineries.. Gas streams that contain significant amounts of H₂S are treated in an amine solution to absorb the sulfide components. The sulfide enters can be recovered in the widely used Claus sulfur-recovery process to SO₂ and water in a reaction furnace. The Claus process involves burning one third of the H₂S with air (6).



The reaction is exothermic. After quenching the hot gases to generate steam, the cooler gases are passed through a sulfur condenser to recover liquid sulfur. (CORINAIR 96)

The remaining uncombusted two thirds of the H₂S reacts with SO₂ to form elemental sulfur (7):



This reaction is exothermic as well. EPA Document AP-42, Chapter 8 contains the following emission factors: 29-65 g SO₂ / kg sulfur. These are post-treatment factors.

80.5.4 Reclaiming sulfur-containing waste (gas aktuell 59)

Another method of producing sulfur dioxide is by cracking used and reclaimed acids and tars. The cracking reactor operated with a coke bed at about 1000 °C cracks sulphuric acid to sulfur trioxide, which is then reduced to sulfur dioxide. Sulfur fumes are totally combusted to SO₂. The cracking facility produces high-grade sulphuric acid and SO₂. The addition of oxygen enhances cracking efficiency. According to (gas aktuell 59) Table 1, the recycling process requires 2421 kcal/kg reclaimed acid without oxygen injection and 1724 kcal/kg reclaimed acid when oxygen is injected into the cracking process. Depending on the composition of the initial waste material, surplus coke can be formed, which can be recycled (US Patent, Grillo-Werke AG).

80.5.5 Removing SO₂ from gas streams

Compression and Condensing of pure or high concentration SO₂ (DKL Liquid SO₂)

At atmospheric pressure, pure SO₂ will begin to condense at -10.1°C. If the gas is compressed to 388 kPa(g) SO₂ will begin to condense at 32.2°C. This temperature is high enough that normal cooling water can be used to condense SO₂.

When the concentration of SO₂ is less than 100%, the gas must be compressed to higher pressures to obtain a high enough condensing temperature to use cooling water as the condensing medium.

Refrigeration of gases containing low SO₂ concentrations (DKL Liquid SO₂)

At low SO₂ concentrations (typically 7-14%), high pressures are required in order to use cooling water to condense SO₂ from the gas. The alternative is using refrigeration. Refrigeration systems can achieve temperatures as low as -55°C. Typically, only 50% of the SO₂ can be condensed from the gas. The tail gas from the refrigeration process is used to pre-cool the incoming gas prior to being directed to some other process, such as a sulphuric acid plant, for further treatment.

Absorption and Acidification of gases containing very low SO₂ concentrations (DKL Liquid SO₂)

Gas containing low concentrations of SO₂ (typically 1-2% vol) is scrubbed using an ammonia solution to form ammonium bisulphite according to the reaction (8):



The ammonium bisulphite solution is reacted to sulphuric acid to form ammonium sulphate, water and SO₂ in reaction (9).



The SO₂ is stripped from the ammonium sulphate solution and is directed to liquid SO₂ production. The gas containing essentially 100% SO₂ is dried using concentrated sulphuric acid. The dried SO₂ gas is compressed and then condensed using cooling water.

80.6 Life cycle Inventory for liquid sulfur dioxide

Due to the lack of substantive data, the following inventory is composed of estimates and assumptions.

80.6.1 Precursor materials

No single precursor material can be given, due to the range of processes that produce liquid sulfur dioxide. For this reason, the process described in chapter 80.5.1 (SO₂ from the combustion of sulfur) is chosen as the representative process. For this process, per mole of sulfur dioxide (64.06 g), one mole of oxygen (32g) and 32 g of sulfur are required.

80.6.2 Energy usage

There was no accurate information available on the amount of energy used for all of the production processes, as some are exothermic, while others require energy.. Therefore, values are approximated with data from a large chemical plant site in Germany producing 2.05 Mt per year (intermediates included) of different chemicals (Gendorf 2000). The values for the energy consumption per kg of product of this plant (3.2 MJ / kg) were used as approximation for the energy consumption of the sulfur dioxide production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory an amount of 2 MJ / kg natural gas and 1.2 MJ / kg electricity was used.

80.6.3 Air emissions

An assumed value of 47 g SO₂ emissions per kg of produced SO₂ is approximated from EPA Document AP-42, Chapter 8. It is furthermore assumed that the electricity required for motors, pumps etc. is released to air as heat.

80.6.4 Wastewater emissions

No information available

80.6.5 Liquid wastes

No liquid wastes are given.

80.6.6 1.6.6 Solid wastes

No information available

80.6.7 Infrastructure

No information on infrastructure was readily available. For this reason, the module “chemical plant, organics” was used as an approximation. This module assumes a production capacity of 50'000 tons/year and a plant life of fifty years, which translates to 0.000000004 units per kg of produced sulphur dioxide.

80.7 Data quality considerations

The data quality is considered to be poor, as the raw materials and energy usage are estimated from industry sources.

The following table summarizes the input and output data as well as the uncertainties used for the production of sulfur dioxide. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 80.11.

Tab. 80.2 Input / output data and data quality for SO₂ production in Europe

Explanations	Name	Location	Unit	sulphur dioxide, liquid, at plant	Uncertainty Type	Standard Deviation 95%	General Comment
	Location			RER			
	Infrastructure Process Unit			0			
				kg			
Input from Technosphere	chemical plant, organics electricity, medium voltage, production UCTE, at grid	RER UCTE	unit kWh	4.00E-10 3.33E-01	1 1	1.22 1.88	(2,2,1,3,1,5); infrastructure of a typical plant (5,5,1,3,4,5); estimation
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.64E-01	1	1.88	(5,5,1,3,4,5); estimated
air emission	secondary sulphur, at refinery	RER	kg	5.50E-01	1	1.64	(4,4,1,3,4,5); assumed precursor
	Sulfur dioxide		kg	4.70E-02	1	1.38	(4,5,1,2,1,5); estimated
	Heat, waste		MJ	1.20E+00			
Outputs	sulphur dioxide, liquid, at plant	RER	kg	1			

80.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

80.9 Conclusions

The inventory for sulphur dioxide is based on theoretical reflections, estimations and assumptions. The unit process raw data are meant to be used as background information if sulphur dioxide is used for a product in small amounts. Therefore these data can only give a rough approximation. They are not reliable enough for direct comparison of this material with other, alternative products

80.10 References

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- EPA Document AP-42 EPA: "Background report AP-42 section 5.18, sulfur recovery", 1996
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- German BAT Notes German Notes on BAT of the Production of Large Volume Gaseous and Liquid inorganic Chemicals. UBA, 4.3.2000

80.11 EcoSpold Metainformation

ReferenceFunction	Name	sulphur dioxide, liquid, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	includes precursor secondary sulfur from refineries and infrastructure. No transports.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Schwefeldioxid, flüssig, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	This inventory is based on numerous assumptions taken from literature. There are many different processes that generate liquid sulfur dioxide, but very little information available.
ReferenceFunction	CASNumber	7446-09-5
TimePeriod	StartDate	1997
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	
Geography	Text	RER
Technology	Text	is an assumption, very little data available
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see technology
Representativeness	Extrapolations	see technology
Representativeness	UncertaintyAdjustments	none

81 Sulphur Hexafluoride

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 Review: Roland Hischier, Rolf Frischknecht

Summary

This section investigates the production of sulphur hexafluoride (SF_6). The inventory is a rough estimation based on information from literature. The inventory of SF_6 production can be considered as a basis for the assessment of this material with the use in technical applications.

81.1 Introduction

This section investigates the production of sulphur hexafluoride (SF_6).

81.2 Production and Use of Sulphur Hexafluoride

The total annual production of sulphur hexafluoride (SF_6) amounts to 8'500 tonnes in 1997. An important producer in Germany is Solvay.⁸ About 1'000 tonnes out of this are produced as a by-product of UF_6 production (see Dones 2003 for details). About 80% of the produced amount is used for SF_6 insulated electrical installations and switchgear manufacturers. The magnesium industry uses 5% of the total production. Sulphur hexafluoride is used for blanketing molten magnesium (Maiss & Brenninkmeijer 1998).

A total of about 6'000 tonnes SF_6 was emitted 1996 into the atmosphere (Maiss & Brenninkmeijer 1998:3079). If SF_6 is used in electrical equipment, the emission occurs sometimes decades after the production, while SF_6 used in e.g. the magnesium industry is emitted shortly after usage. The magnesium industry is a major source of worldwide SF_6 emissions. Production processes for SF_6 are not identified as an important source of emissions (Maiss & Brenninkmeijer 1998:3079). Since a few years efforts have been increased to recycle SF_6 that is used in technical facilities in order to reduce the emissions.

81.3 System Characterisation

Sulphur hexafluoride is mainly produced by burning sulphur in a stream of fluorine (Aigueperse et al. 1999):



81.4 Life Cycle Inventory

Data for the energy use for SF_6 production are not available, but due to the exothermic reaction a low energy use can be assumed. Thus, energy use is not considered in the inventory for SF_6 production. It is assumed that the waste heat of the reaction goes into cooling water. The amount of cooling water used is not known.

The crude gas produced must be purified because it contains SOF_2 , SO_2F_2 , and toxic lower fluorides such as S_2F_2 , SF_4 , and S_2F_{10} . The gases can be washed in a KOH spray scrubber to remove the major portion of the hydrolysable compounds (S_2F_2 , SF_4 , HF, F_2 , SO_2F_2 , etc.). The gas mixture is then passed through a metal tube at 400°C to pyrolyze the S_2F_{10} to SF_4 and SF_6 . Another washing with alkaline so-

⁸ See www.solvay-fluor.de for more information.

lution is necessary to remove the last portions of hydrolysable compounds. The gases next pass through a tower containing a suitable drying material, such as alumina, phosphorus pentoxide, or barium oxide, before being purified over charcoal, distilled, compressed, and transferred to steel cylinders for storage (Aigueperse et al. 1999). The environmental impacts and energy uses for the purification step are not known.

It is assumed for the inventory that SF₆ is produced from secondary sulphur and fluorine. Emissions of SF₆ during production are estimated with 5kg/t.⁹ The standard transport distance for materials has been applied only for sulphur. It is assumed that the production takes place at the same plant as the fluorine production because this product is not easy to transport. Infrastructure is estimated with a generic module. The unit process raw data and data quality indicators are shown in Tab. 81.1.

Tab. 81.1 Unit process raw data and data quality indicators for sulphur hexafluoride production. References and assumptions are presented in the text.

	Name Location InfrastructureProcess Unit	Location	Infrastru	Unit	sulphur hexafluoride, liquid, at plant		Uncertai	Standar	Deviat	on95%	GeneralComment
					RER	0 kg					
output technosphere	sulphur hexafluoride, liquid, at plant	RER	0	kg	1.00E+0		1	1.35 (3,4,2,3,3,5); Other energy carriers possible	1	2.09 (4,5,na,na,na,na); Standard distance 600km	(3,4,2,3,1,5); Literature
	fluorine, liquid, at plant	RER	0	kg	7.81E-1						
	secondary sulphur, at refinery	RER	0	kg	2.19E-1						
	chemical plant, organics	RER	1	unit	4.00E-10						
	transport, freight, rail	RER	0	tkm	1.32E-1						
	transport, lorry 32t	RER	0	tkm	2.19E-2						
emission water, river	Heat, waste	-	-	MJ	7.51E-9		1	1.35 (3,4,2,3,3,5); Literature	1	2.09 (4,5,na,na,na,na); Standard distance 100km	(5,na,1,1,5,na); Rough estimation
emission air, unspecified	Sulfur hexafluoride	-	-	kg	5.00E-3		1	1.35 (3,4,2,3,3,5); Literature	1	2.09 (4,5,na,na,na,na); Standard distance 100km	(3,4,2,3,1,5); Literature

81.5 Data Quality Considerations

Tab. 81.1 shows the data quality indicators for the inventory of SF₆ production. The simplified approach with a pedigree matrix has been used for calculating the standard deviation. The inventory is only a rough estimation for the production process without much specific data about emissions and energy uses.

81.6 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database (www.ecoinvent.ch).

81.7 Conclusions

The inventory of SF₆ production can be considered as a basis for the assessment of this material with the use in technical applications.

⁹ Information provided by Siemens for SF₆ produced by Solvay.

Appendices: EcoSpold Meta Information

ReferenceFunction	401 Name	sulphur hexafluoride, liquid, at plant
Geography	662 Location	RER
ReferenceFunction	493 InfrastructureProcess	0
ReferenceFunction	403 Unit	kg
DataSetInformation	201 Type	1
	202 Version	1.0
	203 energyValues	0
	205 LanguageCode	en
	206 LocalLanguageCode	de
DataEntryBy	302 Person	41
	304 QualityNetwork	1
ReferenceFunction	400 DataSetRelatesToProduct	1
	402 IncludedProcesses	Production of SF6 from fluorine and sulphur. Infrastructure estimated with generic data. No data for energy use.
	404 Amount	1
	490 LocalName	Schwefelhexafluorid, flüssig, ab Werk
	491 Synonyms	
	492 GeneralComment	About 80% of the produced amount is used for SF6 insulated electrical installations and switchgear manufacturers. The magnesium industry uses 5% of the total production.
	494 InfrastructureIncluded	1
	495 Category	chemicals
	496 SubCategory	inorganics
	497 LocalCategory	Chemikalien
	498 LocalSubCategory	Anorganika
	499 Formula	SF6
	501 StatisticalClassification	
	502 CASNumber	002551-62-4
TimePeriod	601 StartDate	1998
	602 EndDate	1998
	603 DataValidForEntirePeriod	1
Geography	611 OtherPeriodText	Time of publication
Technology	663 Text	Estimation for Europe
Representativeness	692 Text	Burning of sulphur in a stream of fluorine
	722 Percent	
	724 ProductionVolume	8500 t in 1997
	725 SamplingProcedure	Literature survey
	726 Extrapolations	From single data.
	727 UncertaintyAdjustments	none
DataGenerator AndPublication	751 Person	41
	756 DataPublishedIn	2
	757 ReferenceToPublishedSource	8
	758 Copyright	1
	759 AccessRestrictedTo	0
	760 CompanyCode	
	761 CountryCode	
	762 PageNumbers	chapter sulphur hexafluoride

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82 Sulphur trioxide

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 Review: Heiko Kunst, TU Berlin

82.1 Introduction

Sulphur trioxide (SO_3 , CAS-No. 7446-11-9) is the anhydride of sulphuric acid. Müller (2000) reports that this substance is known in all three states - in this study, the liquid form is further examined as this is one of the raw materials for the production of dimethyl sulphate.

The most important chemical and physical properties of liquid sulphur trioxide are given in the following table.

Tab. 82.1 Chemical and physical properties of sulphur trioxide (data from Müller (2000))

Property	Value	Sulphur trioxide	Remarks
Molecular weight	g mol^{-1}	80.06	
Density	g cm^{-3}	1.9	at 20 °C
Boiling point	°C	44.8	at normal pressure
Melting point	°C	16.9 - 62.2	selon solid form used

82.2 Reserves and Resources of material

Sulphur trioxide is according to Müller (2000) always produced in sulphuric acid plants, but only in diluted form. More often, it is produced by distillation of oleum. There is no information about the production capacities or the consumption of sulphur trioxide available.

82.3 Use of material / product

Sulphur trioxide is used as educt for sulphonation reactions, i.e. the production of dimethyl sulphate.

82.4 Systems characterization

In the production process for sulphur trioxide the main raw materials, an approximation of the production energy and estimations for the emissions to water and air are included. This module represents therefore only a rough estimation of the process requirements and should be used only for processes where the impact of sulphur trioxide is not considered to be high. The functional unit for the inventory is 1 kg of liquid sulphur trioxide. As process location Europe (RER) is used.

82.5 Sulphur trioxide, at plant (Location: RER)

82.5.1 Process

This dataset includes a rough estimation of the production process of sulphur trioxide from oleum. Due to missing production data this inventory bases on information given in Müller (2000). The emissions to air and water were estimated using mass balance. It was assumed that wastewater is treated in a internal waste water treatment plant. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is quite large.

A typical flow scheme for the industrial production of sulphur trioxide is shown in Fig. 82.1.

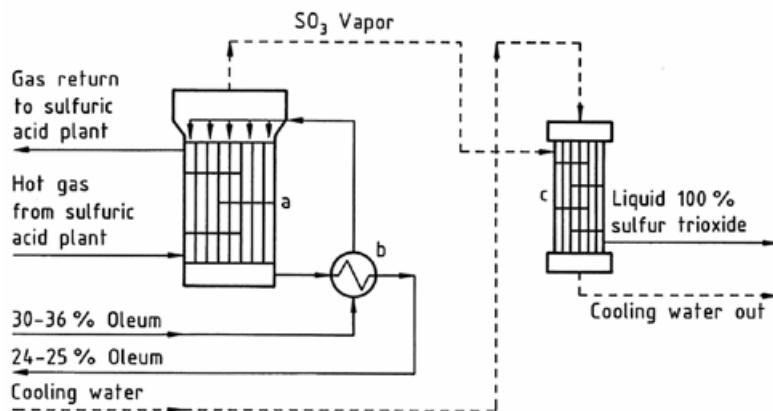


Fig. 82.1 flow scheme for the production of sulphur trioxide by distillation of oleum: a) evaporator, b) heat exchanger and c) SO_3 condenser (Fig. 48 from Müller (2000))

According to Müller (2000) oleum is preheated by hot gas from a nearby sulphuric plant and distilled on a falling-film evaporator. The product is cooled in two stages as well as distilled - resulting in a pure sulphur trioxide.

82.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the wastewater treatment. Fossil fuel is needed to generate the desired heat within the process scheme. There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the sulphur trioxide production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be delivered as hot gas from the sulphuric acid plant "for free" (heat exchange is taking place). Thus, in this inventory only an amount of 1.2 MJ kg^{-1} electricity is shown.

Raw materials

The only input for this process is oleum – a co-product from the sulphuric acid production (see also explications about sulphuric acid production in chapter 83 of this report). According to the sulphuric acid production process, oleum is produced in parallel to sulphuric acid. Thus, to estimate the environmental burdens of oleum, the production burden of the equivalent amount of sulphuric acid is used here as an approximation. Assuming – due to a lack of quantitative information – that 0.5 kg oleum are produced per kg of sulphuric acid, the environmental burdens of 1 kg of oleum equals to the burdens of 0.67 kg sulphuric acid.

For this process here, assuming further an 1:1 synthesis of sodium trioxide out of oleum, a total amount of 2.23 kg oleum are used per kg of sodium trioxide produced. Thus, an input of 1.494 kg sulphuric acid per kg sodium trioxide is added to the dataset here.

Water use

There was no information available on the amount of cooling water used within the plant, although there has to be a respective use. In order not to neglect the process cooling water demand this value was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). In this plant in total an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the ethanolamines production. According to the ongoing IPPC activities of the European Commission, the cooling water demand may reach 86 kg kWh^{-1} for a once through cooling system, which would lead to a cooling water demand of 48 kg per kg product for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m^3 cooling water per kg product was used.

There is no process water us within the process.

Transport

According to Müller (2000), the heating gas as well as the oleum used are from a near-by sulphuric acid plant. Therefore, no transports have to be taken into account.

82.5.3 Emissions

Waste heat

It was assumed that 100% of the electricity consumed is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of sulphur trioxide. As approximation the air emissions occurring from the purge vent, the distillation vent and fugitive emission sources were estimated to 0.2% of the above mentioned raw material input.

This assumption leads to air emissions of 4.45 g of oleum per kg produced sulphur trioxide – reported as 2.4 g sulphate (from sulphuric acid part of oleum) and 1.6 g sulphur dioxide (from the sulphur trioxide part in oleum).

Emissions to water

As there is no use of process water, neither there could be any emissions to water. The cooling water is kept separated from the reaction and therefore got no contamination.

Solid wastes

Solid wastes occurring during the production of sulphur trioxide were neglected in this inventory.

Tab. 82.2 Energy demand, resource demand and emissions for the production of sulphur trioxide

[per kg sulphur trioxide]			Remark
INPUTS			
oleum	kg	2.23E+00	reported as 1.494 kg sulphuric acid
Electricity, medium voltage	kWh	3.33E-01	estimation
Water, cooling, unspecified	m3	2.40E-02	estimation
chemical plant, organics	unit	4.00E-10	approximation for infrastructure
OUTPUTS			
waste heat, to air	MJ	1.20E+00	calculated from electricity input
sulphate, to air	kg	2.40E-03	calculated from output of 4.45 g oleum
sulphur oxides, to air (expressed as SO ₂)	kg	1.60E-03	calculated from output of 4.45 g oleum

82.5.4 Infrastructure

For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg sulphur trioxide was included.

82.6 Data quality considerations

The following table shows the data quality indicators for the inventory of the sulphur trioxide production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the sulphur trioxide production has a high uncertainty, because only few data of the production processes were available. The water consumption and the energy demand were estimated by using an average chemical process as approximation. A higher uncertainty exists even for input of raw materials and the emissions. Due to missing data these values are based mainly on assumptions and approximations (oleum by sulphuric acid as input material). Further uncertainty occurs from possibly missing auxiliary materials and further emissions or wastes. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 82.9.

Tab. 82.3 Input / Output and uncertainty values for the process “sulphur trioxide, at plant (RER)”

Explanation	Name	Location	Unit	sulphur trioxide, at plant RER o kg	uncertaintyType standardDeviation95%	GeneralComment	
						Location	
						InfrastructureProcess Unit	
Resource Input from Technosphere	Water, cooling, unspecified natural origin		m3	2.40E-02	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	sulphuric acid, liquid, at plant	RER	kg	1.49E+00	1	2.32	(5,5,na,na,na,5); estimation
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation
Output Air emission	sulphur trioxide, at plant	RER	kg	1			
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input
	Sulfate		kg	2.40E-03	1	2.32	(5,5,na,na,na,5); estimation
	Sulfur dioxide		kg	1.60E-03	1	2.32	(5,5,na,na,na,5); estimation

82.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

82.8 Conclusions

The inventory for sulphur trioxide is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if sulphur tri-oxide is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

82.9 EcoSpold Meta Information

ReferenceFunction	Name	sulphur trioxide, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Estimated emissions to air from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation) included. Raw materials (2.23 kg oleum) approximated by including an input of the respective amount of sulphuric acid production, based on assumption of 0.5 kg oleum/kg sulphuric acid. Solid wastes omitted.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Schwefelflioxid, ab
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	The functional unit represent 1 kg of liquid sulphur trioxide. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	CASNumber	07446-11-9
TimePeriod	StartDate	2000
TimePeriod	EndDate	2000
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of published literature
Geography	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	Text	Production from oleum by distillation. The emissions to air (0.2 wt.% of raw material input) were split off into sulphate and sulphur dioxide.
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	Extrapolations	
Representativeness	UncertaintyAdjustments	

82.10 References

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http://www.mrw.interscience.wiley.com/ueic/ull_search_fs.html.

83 Sulphuric acid

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 Review: Heiko Kunst, TU Berlin

83.1 Introduction

Sulphuric acid (H_2O_4S , CAS-No. 7664-93-9) is a colorless to yellow, oily, dense liquid with sharp, acrid odor. Sulphuric acid is hygroscopic and miscible in water in all proportions. The most important chemical and physical properties are summarized in Tab. 83.1.

Synonyms for Sulphuric acid: Dipping acid; Hydrogen sulfate; Oil of vitriol; Sulfuric acid.

Tab. 83.1 Chemical and physical properties of Sulphuric acid (ESA-EFMA 2000).

Property	Value	Unit	Property	Value	Unit
Molecular weight	98.0734	$g\ mol^{-1}$	Melting point	-3	°C
Density (at 20°C)	1.84	$g\ cm^{-3}$	Boiling point	270	°C
pH (no dilution)	1		Vapor Density	3.4	°C

The following description of reserves, resources and the use of sulphuric acid are summarized from ESA-EFMA (2000), Patyk (1997) as well as from Wiesenberger (2001).

83.2 Reserves and Resources

The most relevant raw materials used for sulphuric acid production are:

- elemental sulphur
 - obtained as main product from different processes or
 - as by-product from the desulphurisation of crude oil and natural gas.
- pyrite (iron sulphide)
- metal sulphides ores (other than pyrite): ores containing ZnS, CuS or PbS
- sulphates
- sulphur containing gases
- spent sulphuric acids

As can be seen, sulphuric acid production is connected with many other processes: petrochemical and metallurgical processes, as well as other chemical processes that produce spent acids. The production based on smelter gas or spent acid is often done not only to recover the sulphur because of economical reasons but also to avoid air pollution or emission of sulphur-containing wastes. Therefore, the resources available as well as the reserves are related not only to the sulphur in nature but are also linked to other industrial processes with different markets and dynamics.

The total sulphuric acid production in 2000 in Continental Europe totaled 40 Mio tones, from which 19 Mio tones correspond to Western Europe (Micheaux (2002)¹⁰). ESA-EFMA (2000) presents a list

¹⁰ Micheaux (2002): Michaux M., CEFIC-European Chemical Industry Council. Personal communications on 02.07.2002 and 20.08.2002.

of nine western production plants built after 1990 with their corresponding production capacities. These range from 500 to 2400 t.d⁻¹, being the average 1246 t.d⁻¹. Trickett (1995) mentions capacities as high as 3500 t.d⁻¹ for new plants.

83.3 Production Technologies and Use

83.3.1 Production technologies for sulphuric acid

The commercial production of sulphuric acid in Western Europe is achieved by the contact process that includes the following steps:

- First, the sulphur in the feedstock is oxidized (burned) to sulphur dioxide (SO₂):

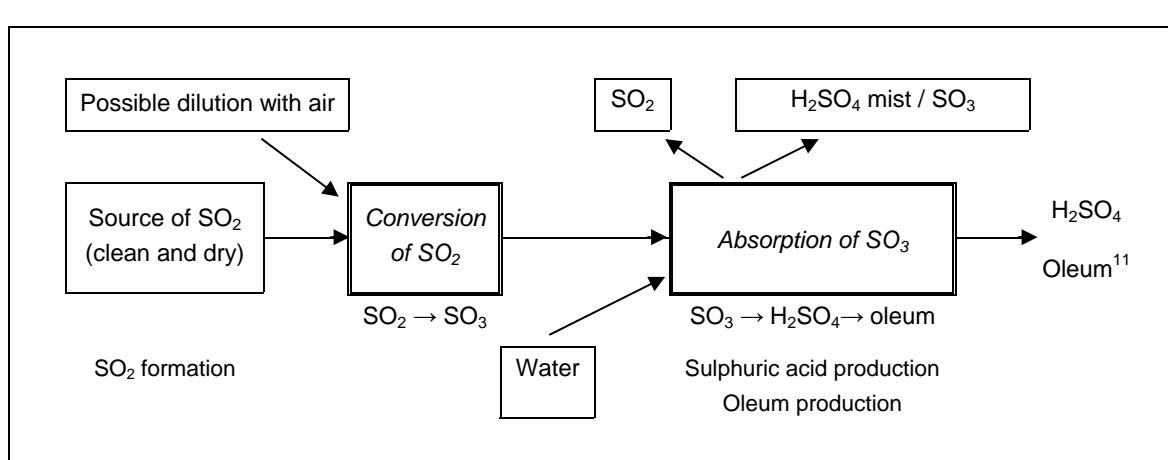
$$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$$
- The resulting sulphur dioxide is fed to a process unit called a converter where it is catalytically oxidized to sulphur trioxide (SO₃):

$$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$$
- Finally, the sulphur trioxide is absorbed in a strong concentrated sulphuric acid solution:

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$$

It is possible to draw a general diagram of sulphuric acid production distinguishing the two fundamental steps of the process:

Fig. 83.1 General diagram of sulphuric acid production (Figure 1 from ESA-EFMA 2000)



1.3.1.1 The contact process

According to this process, SO₂ raw gases are oxidized to SO₃ on catalysts containing alkali and vanadium oxides, at temperatures between 420 °C to 620 °C. This exothermic reaction is accomplished in a contact tower, which usually has 4 to 5 catalyst layers. Gases leaving one of the catalyst layers are cooled by heat exchangers to the inlet temperature of the next catalyst layer. The SO₃ obtained is absorbed in absorbers by concentrated sulphuric acid (or oleum in some cases). In these absorbers, the SO₃ is converted to sulphuric acid by the existing water in the absorber acid. This acid is kept at the desired concentration by adding water or diluted sulphuric acid.

¹¹ Oleum: highly concentrated sulphuric acid (solution of uncombined SO₃ dissolved in H₂SO₄)

Dry contact processes are used for processing raw gases from the burning of sulphur, pyrites or metallurgical off-gases and for processing raw gases from waste acid regeneration processes. SO₃, which is formed by the catalytic process, is cooled and absorbed outside the contact tower in concentrated sulphuric acid. Process technologies differ with regard to the number of absorption steps and to the temperature of the SO₂ inlet gases. The **wet contact process** uses wet gas, in contrast with the conventional contact process in which dry sulphur dioxide/air mixtures are treated. Wet SO₂ gases, e.g. from burning or catalytic conversion of H₂S gases, are directly supplied into the contact tower without previous drying. The SO₃ formed by the catalytic conversion immediately reacts with the moisture of the gases, thereby forming sulphuric acid, which is afterwards condensed.

In **single contact process (single absorption)** SO₃ is absorbed in an intermediate absorber installed after the last catalyst layer. The single contact process is only used in new plants to process SO₂ gases with low (3 to 10%) and widely varying SO₂ contents. In existing single absorption plants the SO₂/SO₃ conversion efficiency is rarely better than 98%; in the new plants it is about 98.5% and can be upgraded to 99.5%. With **double contact process (double absorption)** SO₃ is absorbed in an intermediate absorber installed after the second or third catalyst layer, resulting in considerable higher overall conversion efficiencies. In general, SO₂ feed gases containing up to 12% Vol. SO₂ are used for this process. Conversion rates of about 99.9% are achievable in the case of sulphur burning double contact process when using a 5th catalyst layer or cesium treated catalysts. Practically all new plants constructed are double absorption units.

The so called **Nitrogen Oxides Process**, which in contrast to contact processes uses NO_x as a catalyst in the conversion of the SO₂, is not in operation in Western Europe.

Many variants of contact process for sulphuric acid production have been developed according to the large number of sources of raw materials and their specific characteristics (ESA-EFMA (2000)). Contact plants are classified according to the raw materials charged to them. **The most relevant in Europe are: Elemental Sulphur Burning, Smelter Gas Burning, Pyrites Roasting and Spent Acid Regeneration.**

Production plants built before 1970 were designed on the basis of single absorption process, with associated conversion rates of 96 to 98.5%. Plants built after that time operate the double absorption process with conversion rates of 99 to 99.7%. Large differences exist between these two groups of production plants; mainly depending on the upstream processes generating the SO₂- containing gases.

Some processes (Elemental sulphur burning, for example) generate SO₂- rich and non-variable gases leading to the highest conversion rates. Some others like Spent Acid Regeneration generate SO₂- lean and/or variable gases with corresponding lower conversion rates. In certain cases it is thus impossible to use a double absorption process. In metallurgical plants the conversion efficiency depends on the fluctuations of the SO₂ concentration at the inlet to the plant.

For maximal process efficiency it is necessary to supply a gas with the highest and less variable SO₂ concentration as possible. An adequate O₂/SO₂ ratio is also necessary.

Elemental sulphur burning

Liquid sulphur is obtained from desulphurisation of natural gas or crude oil by the Claus-Process, with the cleaning of coal flue gas as a second source. The third way is the melting of natural solid sulphur (Frash-Process) but this is not in frequent use due to the difficulties in removing the contaminants. Elemental sulphur is delivered in solid or liquid state. When the sulphur has a high content of ashes, it is filtered (in liquid state) before burning to avoid damages in the installation caused by the ashes. The sulphuric acid production process based by means of elemental sulphur burning begins with the highly exothermic combustion of sulphur to SO₂. The combustion is carried out at between 900 and 1800 °C in one-stage or two-stage sulphur combustion units, each unit consisting of a combustion chamber followed by a process gas cooler. The energy obtained from the combustion is mainly used for steam generation. The SO₂ content of the combustion gases is generally up to 18% by volume and the O₂ is

low (but higher than 3%). The gases are generally diluted to 10-11% before entering the conversion process.

Pyrites roasting

Pyrite, or iron sulphide, can also be used for sulphuric acid production. The sulphur content in pyrites vary between 30 and 50% w/w. Pyrite is roasted in various types of furnaces, e.g. multiple-hearth furnace, rotary kiln and fluid bed roaster, producing a gas with a somewhat lower sulphur dioxide content than the combustion gases from burning elemental sulphur. This gas is then diluted to 8-10% sulphur dioxide, dried and cleaned before entering conversion. The gases are always treated in 3-4 cleaning steps using cyclones, bag filters, scrubbers and electrostatic precipitators with a Whig efficiency. The SO₂ content in the gases is slightly variable over time due to the heterogeneous character of the raw material.

Here, the sulphur dioxide is the main product and the iron oxide is the by-product. The sulphuric acid production based on pyrites roasting is of little importance comparing to other production processes, because the utilization of the burning for the production of iron is not cost-efficient enough.

Smelter gas burning:

Many metals sulphides (other than pyrites) when roasted during metallurgical processes produce gases containing SO₂ which can be used to produce sulphuric acid. The SO₂ content in the process gas obtained from the mentioned processes varies from 1 to 13%, depending on the type of ore. The most relevant ores for the production of sulphuric acid are those containing ZnS, CuS or PbS. There are different metallurgical processes in use, according the ore concentrate.

The first step in the sulphuric acid production process from smelter gas is the cleaning of the SO₂ raw gas, what is very demanding because of the high content of dust in it. Hence, the sulphuric acid production based on smelter gas depends basically on the extraction of metals like Copper, Lead or Zinc from sulphidic ores. Here, the sulphur dioxide is a by-product and the metals are main products.

The average SO₂ content in the smelter gas and its variability in time is different according to the ore-concentrate burned. The concentration of SO₂ in the gases entering the plant determines the amount of gas that must be treated per tone of fixed sulphur. For this reason the size of the plant and the cost of fixing the sulphur increase as the concentration of SO₂ dismisses. The double absorption is largely used, particularly when SO₂ concentrations are high and constant.

Spent acid regeneration

Spent acids come mainly from organic chemical production, where H₂SO₄ is mostly used as a catalyst and needs to be replaced with fresh concentrated acid when diluted and/or saturated with organics. Alkylation processes in refineries and nitration and sulphonation processes in the chemical industry generate large amounts of spent acids which, after regeneration, became clean acid which can be recycled in any process. Thermal decomposition of spent sulphuric acids to give sulphur dioxide is achieved in a furnace at temperatures around 1,000 °C.

The SO₂ content in the gases mainly depends on the composition of the spent acids. The water and organics contents may affect the gas composition. Sulphur, pure or waste can generally be added to adjust the SO₂ content.

The most part of the energy from the combustion gases is recovered as steam in a Waste Heat Boiler. Downstream, the gases are cleaned, demisted and dried before going to the converter. Upstream of the converter, the gases are reheated to the ignition temperature through gas/gas heat exchangers using the conversion heat. Double absorption is considered as the best available technology for new plants. Nevertheless, a double contact process can be used only if the SO₂ content of the gases is high enough (about 8%) at the converter inlet.

Other contact processes

Since the oxidation of SO₂ is favored by pressure, pressure contact processes have been developed in which SO₂ conversion and SO₃ absorption are both achieved at high pressure. This kind of process has comparatively a higher conversion rate, but it also produces more emissions and it requires higher inversion costs for equipment.

Other contact processes implying different sources of sulphur than the mentioned above are also in use, although they do not contribute significantly to the total production and therefore are not considered in this study. They are the sulphate roasting, the tail gas scrubbing and the combustion of sulphur containing gases from other process than ore burning.

ESA-EFMA (2000) reports on a process recently developed in Russia known as „unsteady state oxidation process,, that is based on a periodical reversal of the direction of the reaction mixture flow over the catalyst bed. This single bed process has the advantage of being able to treat gases with low and variable concentrations of sulphur dioxide, without much of the heat exchange equipment associated with other processes. There are several developments to improve the gas-cleaning step and thus minimize the SO₂ and SO₃ emissions.

1.3.1.2 Quality of the final product sulphuric acid

Impurities in the final product sulphuric acid can arise from two sources: contaminants in the feedstock, and those resulting from corrosion of plant equipment. As the purity of sulphur fed to most sulphur burning plants is high; the acid product from these plants is usually better than the product from either metallurgical acid or spent acid regeneration. In the latter, the quality of the product acid is dictated by the performance of the gas cleaning systems.

1.3.1.3 Conversion rates

The conversion rate indicates the efficiency of converting SO₂ to SO₃. The emissions contain SO₂ and SO₃ depending on this conversion rate. The more efficient the conversion, the less SO₃ generated. According ESA-EFMA (2000), the Contact Process based on Elemental Sulphur Burning has an average SO₂/SO₃ conversion rate of 99.0%. Wiesenberger 2003¹² considers this value too low. According ESA-EFMA (2000), if using Pyrites Roasting, the rate is 99.5% and for Smelter Gas Burning and for Spent Acids Regeneration the conversion rates are 99.1% and 98.6%, respectively.

1.3.1.4 Auxiliary processes before / after sulphuric acid production

Gas cleaning of metallurgical off-gases

The gases containing SO₂ from all metallurgical processes are cleaned before the contact process to remove impurities like fumes or aerosols, volatile gaseous metals and compounds and gaseous non-metallic compounds. After cleaning, small amounts of impurities are absorbed in sulphuric acid or emitted with the tail gas. CO is oxidized to CO₂ in the contact process.

Product finishing

The acid produced, normally 95.5% to 96.5% or 98.5% to 99.5%, is diluted with water or steam condensate down to the commercial concentrations: 25%, 37%, 48%, 78%, 96% and 98% H₂SO₄. In order to reduce the remaining SO₂ in the acid to less than 20 mg SO₂.kg⁻¹, air is blown through the warm acid in a column or tower. This air containing SO₂ is returned to the process. Another step in the product finishing is the denitrification of the acid **or the oleum** with different methods and reactants. Additionally, sulphuric acid produced from smelter plants or acid regeneration plants undergo a decolourisation

¹² Wiesenberger H. (2003) Federal Environment Agency - Austria. Personal communication on 06.06.2003

sation or „acid bleaching“ to remove hydrocarbons or carbonaceous material absorbed in the acid causing a black color in it.

83.3.2 Use

More sulphuric acid is produced than any other chemical in the world. The annual production worldwide is estimated in 160 Mio tones, out of which 40 Mio tones are produced in continental Europe. Western Europe produced in 2000 19 M.t. All European countries are producers, the majors being Germany, Spain, Belgium and Italy.

Sulphuric acid is used in nearly all industry and is a vital commodity in any national economy. Most of its uses are actually indirect in that the sulphuric acid is used as a reagent rather than an ingredient. The largest single sulphuric acid consumer by far is the fertilizer industry. There sulphuric acid is used with phosphate rock in the manufacture of phosphate fertilizers and smaller amounts are also used in the production of ammonium and potassium sulphate. Substantial quantities are used as an acidic dehydrating agent in organical chemical and petrochemical processes, as well as in oil refining. In the metal processing industry, sulphuric acid is used for pickling and descaling steel; for the extraction of copper, uranium and vanadium from ores; and in non-ferrous metal purification and plating. In the inorganic chemical industry, it is used most notably in the production of titanium dioxide.

Certain wood pulping processes for paper also require sulphuric acid, as do some textile and fibbers processes (such as rayon and cellulose manufacture) and leather tanning. Other end uses for sulphuric acid include: effluent/water treatment, plasticisers, dyestuffs, explosives, silicate for toothpaste, adhesives, rubbers, edible oils, lubricants and the manufacture of food acids such as citric acid and lactic acid.

Probably the largest use of sulphuric acid in which this chemical becomes incorporated into the final product is in organic sulphonation processes, particularly for the production of detergents. Many pharmaceuticals are also made by sulphonation processes.

83.4 System characterization

This report corresponds to the module in the Ecoinvent database for the **production of 1 kg sulphuric acid, liquid, at plant, in Europe**.

In Western Europe sulphuric acid is exclusively produced by the contact process and therefore this is the production process considered in this study. The most relevant contact processes are the Elemental Sulphur Burning and the Smelter Gas Burning. Their contributions to the total acid production are 50% and 35% respectively. Pyrites Roasting and Spent Acid Regeneration are of less importance, representing 8.5% and 5.5% respectively of the total production. (Michaux (2002))

For this study data from the above mentioned modalities of the contact process are used to calculate a balanced average value when this is possible. Data from literature referring to the average European sulphuric acid manufacture are also taken. If information is not clear regarding the process involved it is assumed also as an average value. Data regarding processes with little relevance to the European overall sulphuric acid industry are preferably not used.

For this study, according to ESA-EFMA (2000), a production of 1500 t.d⁻¹ will be considered standard. A typical plant size is 1000 to 1500 t.d⁻¹; 8000 t.d⁻¹ or above are common for new plants. Wiesenberger (2001) reports on the production capacities of five Austrian manufacturing plants, ranging these capacities from 14 to 690 t.d⁻¹, quite below the mentioned range in ESA-EFMA (2000). Nevertheless, in Wiesenberger (2001) a production capacity of 1000 t.d⁻¹ is mentioned as standard. It must be noticed that the last mentioned source also includes tail gas processes, aiming at emission abatement of waste gases arising from other industrial processes. Production capacities of these tail gas processes cannot be compared to sulphur burning capacities.

Most acid plants produce sulphuric acid with strength in the range of 93 to 98%. Nevertheless, for this study **all data are referred to 1 kg 100% sulphuric acid**.

The system includes the process starting with sulphur-containing raw materials (elemental sulphur, pyrites, other ores and spent acids), plus consumption of auxiliaries, energy, infrastructure and land use as well as the transportation of the raw materials, auxiliaries and wastes. It also includes the generation of solid wastes and emissions to air and water. It does not include transportation of the final product sulphuric acid. Due to lack of information, the production of oleum is not considered in this study. Thus, for the purpose of this study, there are no coproducts or byproducts generated in the manufacturing process.

Since the sulphuric acid can be considered a byproduct from the processing of sulphide ores (other than pyrites), for this study it is considered that the sulphuric acid produced by smelter gas burning is obtained „gratis“. As mentioned above, this process contributes with 35% to the total production. Consequently, in order to subtract the contribution of this process to the overall average, **all the values for inputs and outputs presented in this study are balanced by multiplying them by 0.65 for the tables in ecoinvent database**. The resulting balanced values are presented in Table 1.6.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorized as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers. Wastes are assumed to be sent to landfill.

83.5 Sulphuric acid production processes

83.5.1 Data sources

Main data source are ESA-EFMA (2000), Müller (1994) and Patyk (1997). Additional data sources are Wiesenberger (2001), Wiesenberger (2003), Davis (1999), KCL (2002), EMEP/CORINAIR (2001), and Habsatter *et al.* (1998). VDI (1984) and UNEP (1998) have been taken into account for plausibility checks and comparison reasons.

ESA-EFMA (2000) is a report on the best available techniques (BAT) for sulphuric acid production prepared in response to the proposed EU Directive on Integrated Pollution Prevention and Control (IPPC Directive). The survey covers Western Europe and represents ca. 35 manufacturing companies that operate in W.E., with an unreported total number of manufacturing sites. Data mentioned are measured data from company sources and represent the figures for state of the art plants. There may be less favorable in older plant under modernization. The document represents therefore a summary of information about present state as well as future improvements possible of the mentioned industry. The booklet was reviewed and updated by EFMA experts drawn from member companies.

Patyk (1997) analyses the material flow and the energy balance of different fertilizers, considering the situation in Germany, East Europe and the EU by analyzing a broad spectrum of sources, like government reports, and diverse literature. Based on these sources and on his own calculations he presents tables with values for inputs and outputs from different fertilizer production processes. The disadvantage of this very complete source is that most of the information proceed from literature and not from recent data from nitric acid plants. For this study his data referred to the EU are analyzed.

KCL (2002) is a Finnish lifecycle inventories database. KCL is a Finnish pulp and paper research company. For sulphuric acid manufacture it presents values based on literature data from the Swedish Pulp and Paper Institute (STFI), from 1996, scored by STFI with reliability 2 (min 1, max 5) and completeness 3. KCL 2002 refers to manufacturing processes currently used in Finland and Sweden but it

is applicable to the average European situation (Wessman (2002)¹³). Besides, KCL did some cross-checking with data provided by manufacturers and even if this information is not available it contributes to validating the values published in the mentioned study (Wessman (2002)).

Davis (1999) is a Compilation of Life Cycle Inventories of different fertilizer products used in Sweden and Western Europe. This survey provides with data based on measurements at manufacturing plants and considers also literature data.

Wiesenberger (2001) considers the actual situation in Austria. The report contains besides theoretical achievable values, real data from five Austrian manufacturing plants in operation in 2001, with different production processes. The disadvantage of this highly reliable source is that since it only reports on values from Austrian production plants, it is difficult to say how representative the data are for the whole European scenario. This source analyses the environmental aspects related to the manufacturing process of sulphuric acid considering both the contact process as well as the previous processes for the generation of SO₂ gases. Wiesenberger 2003 is a personal communication that contributes with helpful additional comments about the sulphuric acid industry.

EMEP/CORINAIR (2001) is a guidebook prepared by expert panels and is intended for general reference and also to be used as source material for emission inventory compilation. They provide what they consider the best current available information, taking into account the European situation. This survey analyses the emissions released from all process steps within the manufacturing plant, based on literature data. They include the production of SO₂ and also of oleum.

Habersatter *et al.* (1998) is a report from a serie of inventories from the Swiss Agency for the Environment, Forests and Landscape (SAEFL). It bases on datasheets provided by the German manufacturing company Lurgy. Data are from the year 1995.

Müller (1994) is a survey included in Ullmann's Encyclopedia of Industrial Chemistry. It is written by a technical expert of a German sulphuric acid manufacturing company, basing on the corresponding article Ullmann 4th ed. It provides with data about energy and mass balances regarding different contact processes.

VDI (1984) is a German study performed by experts from the German Engineers Association, which aims at providing guidelines for decision-makers. They present achievable emission levels for SO₂ and SO₃ considering the state of the art in the manufacturing industry. It is used in this study as a reference.

UNEP (1998) has also the purpose of "providing guidelines". It does not mention its sources of information. Consequently, the values presented in this source were considered principally reference values.

When information in the data sources is presented in ranges of values an average is taken and the amplitude of the range is indicated in the form of percent variability ($\pm\%$).

83.5.2 Raw materials and auxiliaries

As mentioned above, several processes are used to convert the different raw materials into the SO₂ necessary for the contact process. Nevertheless, once the SO₂ has been obtained the process is very similar in all cases. Consequently, the requirement of sulphur contained in the gas is also very similar same for all processes.

The following table gives an overview of the information about the consumption of raw materials containing sulphur in the different sources used.

¹³ Wessman (2002). H. Wessmann KCL. Personal communication on 13.09.2002.

Tab. 83.2 Sulphur containing raw materials consumption for the production of sulphuric acid

(kg.kg ⁻¹ 100%H ₂ SO ₄)	Elemental Sulphur	Zinc-ores	Pyrite	Unspecified (expressed as Sulphur)
Wiesenberger (2001)	~ 3.30 E-01			
Habersatter <i>et al.</i> (1998)	3.30 E-01			
Patyk (1997)			5.00 E-01 ¹	
KCL (2002)	3.28 E-01			
Davis (1999)			7.60 E-01 ²	3.28 E-01
UNEP (1998)	3.30 E-01	1.20 E+00 ¹		
This study	3.30 E-01	1.20 E+00	7.60 E-01²	3.28 E-01

¹: sulphur content not reported²: sulphur content: 48%

For this study, the input of the principal raw material is considered to be 100% elemental sulphur, being the average value 3.30 E-01 kg.kg⁻¹ 100%H₂SO₄. If using pyrites, other ores or spent acids, the input of raw material is as variable as the composition and therefore the sulphur content of the mentioned materials. Thus, in this study we refer to elemental sulphur and for other raw materials the input has to be calculated depending the specific sulphur content and taking into consideration the above mentioned input of sulphur.

Regarding auxiliaries, the different sources mention catalysts as the main auxiliary material in the production of sulphuric acid. Vanadium pentoxide (V₂O₅) is the active ingredient used in all commercial catalyst since fifty years ago. Catalysts contain usually 6% to 9% V₂O₅ with smaller amounts of alkali metal sulfates and a support of porous silica. Nevertheless, there are no values available regarding catalysts consumption in the sources used.

Regarding water, KCL (2002) mentions an input of water of 7.50 E-02 m³.kg⁻¹ 100%H₂SO₄ for elemental sulphur burning (data from 1996; European average technology; valid areas: Finland and Sweden). ESA-EFMA reports a water consumption of 1.00 E-04 m³.kg⁻¹ 100%H₂SO₄ for copper smelter burning. Due to the lack of other information in the sources available, the highest value is taken.

83.5.3 Energy and transportation

Energy

The input of the starting materials also provides thermal energy for the production of sulphuric acid. The manufacture of sulphuric acid is in general self-sufficient regarding energy, except in the case of processes based on waste acid or metal sulfates that are endothermic. An input of electricity is also necessary for ventilator supply of combustion air for all starting materials - excluding waste acid and metal sulfates.

The production of sulphuric acid normally produces more energy than is used in the process. Both the production of SO₂ gas by means of the burning of sulphur, pyrites or sulphidic ores, as well as the conversion of SO₂ into SO₃ are exothermic reactions which generate thermic energy. Super heaters, steam boilers, steam turbines, water preheaters, etc. can be used to gain energy from the process. The heat evolved is used to produce steam and, using combined heat and power generation, electricity. In case of Sulphur Burning Process in conjunction with double absorption, the most energy efficient process, up to 67% of the process waste heat are recovered as high-pressure steam from burning gases and from reaction heat of the contact process. A thermal efficiency of 85 to 90% can be obtained by using waste heat released from the cooling of acid for drying processes and for the production of low-pressure steam. In a highly efficient, modern plant based on sulphur burning, up to 6 MJ per kg 100% H₂SO₄ produced can be gained (Wiesenberger (2001), quoting Kongshaug (1998)).

Waste acid regeneration processes and decomposition of metal sulphates are characterized by rather high energy consumption. When the starting materials are concentrated, preheated and predried the energy consumption is reduced.

If gas cleaning processes are required (e.g. metallurgical off-gases), the cold raw gases are reheated to the reaction temperature of the catalyst by using waste heat from the contact tower. From acid cooling low-level energy is released, which can be used for drying processes or for the production of low-pressure steam.

Habersatter *et al.* (1998) mentions that there is no input of energy in the process but this survey does not mention any energy output, probably because the generation of steam is considered a byproduct of no interest for the purpose of the study.

Patyk (1997) mentions for the production of 1 kg sulphuric acid also an input of 4.90 E-03 MJ from diesel fuel (or 1.14 E-04 kg, according to Frischknecht *et al.* (2003b)) and 2.69 E-02 kWh electricity.

Tab. 83.3 gives an overview of the energy balance in the different sources available. Since steam production is reported in Ecoinvent in MJ as waste heat, values are converted considering that 1 kg of steam corresponds to 2.75 MJ (Boustead (1999)).

Tab. 83.3 Energy balance for the production of sulphuric acid in the different processes.

MJ.kg ⁻¹ 100% H ₂ SO ₄	Wiesenberger (2001)	UNEP (1998)	Patyk (1997)	The Royal Society of Chemistry	ESA-EFMA (2000)	Müller (1994)	This study
Elemental Sulphur Burning	-5.60 E+00 ¹ -2.60 E+00 ²	-3.16 E+00 ^{1,3} (± 5%)	-3.60 E+00 ^{1,4} -1.60 E+00 ^{2,4}	-3.71 E+00 ^{3,5} (± 4%)	-2.50 E+00 -3.40 E+00 ⁶ (± 80%) -4.50 E+00 -2.50 E+00	-5.40 E+00 ⁷ -3.71 E+00 ⁸ - 2.7 E+00 ⁷	-5.60 E+00 -3.40 E+00 -4.50 E+00 5.00 E+00
Smelter Gas Burning							
Pyrites Roasting							
Spent Acids Regeneration			5.00 E+00				

s.a.: single absorption; d.a.: double absorption

(-) indicates that the value correspond to an output

¹ includes the burning of sulphur. Taken from Tab.2.5.

² does not include the burning of sulphur. Taken from Tab.2.5.

³ originally informed as kg steam. Conversion in MJ considering that 1kg steam= 2.75 MJ (Dones *et al.* 2003)

⁴ quoting Müller 1994, but considering another conversion factor for kg steam to MJ. The source consideres steam for export

⁵ for modern plants

⁶ average of values for roasting of different ores (Zn, Cu, Pb-containing ores).

⁷ overall energy output (heatwaste and steam for export)

⁸ steam for export

Davis (1999) quotes Patyk (1997) and consequently, their values are not presented in the table. They present a balancing value of -1.1 MJ .kg⁻¹ 100% H₂SO₄, considering this as average for the production of sulfuric acid in Western Europe. Patyk (1997) presents also for West Europe an average value for steam balance of -7.70 E-01 MJ .kg⁻¹ 100% H₂SO₄, taking the different types of production processes into consideration. Both sources consider in these numbers the steam export and not the waste-heat in the process. To the value given by Patyk 1997 the heat waste due to electricity could be added by using the number given by this source for electricity input.

In Table 1.3 it can be seen that there are differences between the sources used in regard to the energy output for the same type of production process. The reason for this can be that Müller (1994) and Wiesenberger (2001) take the overall energy balance into consideration, including waste-heat and steam for export, while the other sources seem to consider only the usable steam for export. For this study, the first mentioned criterion is shared and thus, the numbers of these sources are considered.

The value for spent acid regeneration from ESA-EFMA does not seem reliable since according to literature this is an energy-consuming process. The value reported –and carefully fundamented- by Patyk (1997) is therefore taken into account for this study.

There are significative differences depending the manufacturing process envolved. Consequently, for this study, a balanced average is calculated, considering the share of the four principal production process to the overall European sulphuric acid manufacturing. As mentioned in section 1.4, these shares are: 50% for Elemental Sulphur Burning, 35% for Smelter Gas Burning, 8.5% for Pyrites Roasting and 5.5% Spent Acid Regeneration. Thus, considering that this steam output is heat-waste and therefore an emission to air, the highest values for each process are taken according to a conservative criterion. The resulting balancing value is $-4.14 \text{ E-01 MJ .kg}^{-1}$ 100% H_2SO_4 . This steam output is reported in ecoinvent as waste heat.

Even if the steam export is not reported as such in ecoinvent, this amount of “useful“ steam should be nevertheless kept in mind: about $3.50 \text{ E+00 MJ .kg}^{-1}$ 100% H_2SO_4 , if using sulphur burning.

Tranportation

Concerning transportation of raw materials and auxiliaries, no information about distances is available in the examined data sources. Therefore, for all raw materials and auxiliaries, standard distances as defined in Frischknecht *et al.* (2003b) were used: 100 km by lorry 32t and 600 km by train. For the transportation of the different wastes produced within the process it is assumed that they are sent to landfill and, again, standard distances are used: 10 km by lorry to disposal site. Additionally, it is asumed that this lorry has a capacity of 32 tonnes in order to facilitate the calculations of the total transport amounts for the database.

For the purposes of the calculation of transport amounts of raw materials, the amounts in kg of raw materials are taken from UNEP (1998) (see section 1.5.2, Tab 1.2) and these values are balanced according the share of the corresponsing process to the total. Spent acids are not taken into account because their composition is very variable and the regeneration process contributes in any case with just a very low percent to the total. Thus, for the production of 1 kg sulfuric acid, $1.53 \text{ E-01 kg sulphur}$, $6.00 \text{ E-02 kg pyrites}$ and $3.91 \text{ E-01 kg zinc ores}$ are considered. This yields $6.04 \text{ E-01 kg raw materials}$. This value is a rough approximation and is only used for the calculation of transport amounts.

Tab. 83.4 summarizes the total transport amounts for the production of 1 kg of 100% sulphuric acid.

Tab. 83.4 Total transport distances and means for the production of weak nitric acid.

(t.km. kg ⁻¹ 100% HNO ₃)	lorry	train
raw material	6.04 E-02	3.62 E-01
auxiliaries	nd	nd
waste to disposal sites	2.50 E-07	0
Total transports	6.04 E-02	3.62 E-01

nd: no data available

83.5.4 Infrastructure and land-use

There is no information available about infrastructure and land-use of sulphuric acid plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. This estimated value is 4.E-10 unit. kg⁻¹ chemical.

83.5.5 Emissions to air and water

1.5.5.1 Emissions to air

All the sources consulted mention almost the same emissions. According to Wiesenberger (2001), SO₂ and SO₃ (H₂SO₄ aerosols) are the major air emissions of the contact process.

NO_x, CO, CO₂ and VOC emissions can be released during the production of the SO₂ raw gases, before the contact process. Gases of pyrite burning, metallurgical off-gases and gases of waste acid regeneration processes contain pollutants such as particulate matter, volatile substances (As, Se, Cd and Hg) and gaseous substances (HCl, HF, AsO₃) which are separated before the contact process. These substances are released via roasting residues, fine dusts, scrubbing residues and sewage.

Emissions of SO₂

The formation of SO₂ results from incomplete oxidation of SO₂ to SO₃ on the catalyst. SO₂ which is not converted into SO₃ is hardly absorbed into water. Hence, SO₂ emissions are dependent on SO₂ content of the raw gases and on the conversion rate of the contact process (the better the conversion efficiency the lower the SO₂ emission). The conversion rate of the contact process depends on the process (e.g. single contact process or double contact process) and on the design of the plant (e.g. number of catalyst layers, kind and quantity of catalyst). Also operating characteristics such as working temperature, O₂/SO₂ ratio and time rate of change of the SO₂ content in the reaction gas are relevant for the conversion rate.

EMEP/CORINAIR (2001) mentions also other SO₂ emission sources (beside the converter): the cleaning of SO₂ raw gas, the final absorbing tower and the scrubbers.

Wiesenberger (2001) reports besides actual values of manufacturing plants also theoretical achievable SO₂ emission levels when applying reduction processes. For integrated process measures for SO₂ emissions this source mentions achievable levels of up to 6.51 E-04 kg.kg⁻¹ 100% H₂SO₄, and for end of pipe reduction measures, 2.17 E-04 kg.kg⁻¹ 100% H₂SO₄ (taking the operational parameters mentioned in the source and assuming that plants work 24 hours 365 days in a year). Nevertheless, these values do not represent necessarily the actual situation in the whole European industry.

Emissions of SO₃ and H₂SO₄ mists

In dry contact processes the formation of SO₃ emissions and H₂SO₄ mists takes place due to an incomplete absorption. An inadequate design of the absorption tower and of the condenser also enhances the formation of SO₃. H₂SO₄ vapor may arise from scrubbing too. In order to minimize SO₃ (H₂SO₄) emissions, dry contact processes require the use of sulphur with low impurity contents and adequate drying of the combustion air (processes based on sulphur burning) and adequate drying of the SO₂ gases (other processes for the production of SO₂ gases). According to EMEP/CORINAIR (2001) large quantities of sulphuric acid mist may be formed by the combustion of hydrogen sulphide and during decomposition processes.

For this parameter Wiesenberger (2001) reports theoretical achievable SO₃ emission levels when applying reduction processes, being this values 20 to 30 mg/Nm³, which means 4.34 to 6.51 E-05 kg SO₃ .kg⁻¹ 100% H₂SO₄ (with the same operational parameters and assumptions as for SO₂ mentioned above).

Emissions of SO_x

Regarding the emission of sulphur oxides, EMEP/CORINAIR (2001) states that even if nearly all sulphur dioxide emissions are found in the exit stack gases, there are other small sulphur oxides emissions sources, like storage tank vents as well as from tank truck vents during loading operations, sulphuric acid concentrators and leaks in process equipment. Few data are available on the quantity of emissions from these non-stack sources

Emissions of VOC, CO and CO₂

Emissions of VOC, CO and CO₂ arise from metallurgical processes (metallurgical off-gases) and from waste acid regeneration processes. Metallurgical processes may cause emissions of dioxines due to the charging of secondary raw materials.

Emissions of Nitrogen Oxides (NO_x)

NO_x emissions have to be considered when elemental sulphur or gases containing sulphur are burnt at higher temperatures and when thermal decomposition of waste acids or waste gypsum takes place. Nevertheless, EMEP/CORINAIR (2001) considers that the emissions of NO_x, CO, Non Methane Volatile Organic Compounds (NMVOC) and ammonia are negligible in the manufacturing process of sulphuric acid

Other Emissions to air

Other emissions mentioned in Wiesenberger (2001) are:

- Particulate matter, which arises at the roasting of pyrites or other ores and at smelting- and refining processes.
- Volatile substances like Arsenic, Selenium, Cadmium and Mercury originated by the roasting of pyrites or other ores.
- Vapors of volatile metal oxides and -chlorides also originated by the roasting of pyrites or other ores.
- Hydrochloric acid, hydrofluoric acid and the already mentioned emissions of CO and VOC, generated at the processing of spent acids, the burning of pyrites or in the non-lead metal industry.

1.5.5.2 Emissions to water

Regarding wastewaters, Wiesenberger (2001) and Patyk (1997) mention emissions arised from diverse gas cleaning processes (especially from cleaning metallurgical off-gases). The first source also mentions wastewaters from diffuse emissions due to leakage, which are collected in collection basins. According to UNEP (1998), liquid effluents arise only from boiler blow-down and water treatment, excepting in case of pyrites burning, by which also effluents from gas scrubbing are generated. No numbers regarding volumes of wastewaters are available in the sources used.

Since the principal emissions to air from the contact process (SO_2 and SO_3) are similar for the different modalities (sulphur burning, pyrites roasting, etc), no difference is made and all information available is considered together.

Available information about emissions to air and water is summarized in Tab. 83.5.

Tab. 83.5 Emissions to air and water of the production of sulphuric acid.

(per kg 100% H ₂ SO ₄)	Haberset-ter et al. 1998 ¹	KCL 2002 ^{1,2}	Trickett 1995 ^{1,3}	VDI 1984	EMEP/ CORINAIR 2001 ⁴	Davis 1999 ⁵	EPA 1995	Wiesen-berger 2001	UNEP 1998 ⁶	Patyk 1997 ⁷	ESA-EFMA 2000	This study
<i>Emission to air</i>												
SO ₂ kg	2.00 E-03	8.30 E-03	2.00 E-03	7.38 E-03 (± 100%)	8.77 E-03 (± 90%)	5.00 E-03	7.00 E-03 ⁸	1.75 E-03 ⁹ 6.75 E-03 ¹⁰	6.75 E-03 (± 80%)	4.92 E-03	5.92 E-03	8.77 E-03
SO ₃ kg	3.00 E-03			3.36 E-04 (± 70%)	3.69 E-04 (± 60%)	3.00 E-04		4.75 E-05 ⁹ 0.15 E-05 ¹⁰	3.75 E-04 (± 60%)		9.94 E-05	3.75 E-04
SO ₃ + H ₂ SO ₄ mist (as H ₂ SO ₄) kg			7.50 E-05									2.00 E-04
SO ₄ ²⁻ kg					2.00 E-04						6.48 E-03	6.48 E-03
SOx (as SO ₂) kg					6.42 E-03 (± 20%)							6.42 E-03
NOx (as NO ₂) kg	7.50 E-04											7.50 E-04
Particulate matter kg										3.50 E-07		3.50 E-07
HCl kg										2.00 E-09		2.00 E-09
NH ₃ kg										1.30 E-08		1.30 E-08
<i>Emission to water</i>												
wastewater m ³	1.00 E-03											1.00 E-03
inorg. diss solids kg	1.50 E-03											1.50 E-03
suspended solids kg	1.50 E-03											1.50 E-03
H ₂ SO ₄ kg		4.00 E-04										4.00 E-04
SO ₄ as ions kg		2.00 E-04										2.00 E-04

cp: contact process; s.a.: single absorption; d.a.: double absorption

When a value is an average of data from the source, the amplitude of the range of the original values is indicated as (±%)

¹ Survey consideres specifically the production by means of elemental sulphur burning.

² Data from 1996, corresponding to an average European technology.

³ For a double contact plant, with a conversion rate of 99.7%. Reported as allowable emission limit, achievable for modern plants. It includes the production of the SO₂ raw gas from Sulphur

⁴ Average from values presented in Table 2 from the mentioned source, which contains numbers for single absorption and double absorption contact processes and spent acid regeneration, extracted from CORINAIR 1992¹⁴, VDI 1984, Bol and Kohnen 1993¹⁵ and Froste et al. 1995¹⁶. Values include the production of the SO₂ raw gas.

⁵ Values considered representative for Western Europe, basing on UNEP 1998.

⁶ It does not include the production of the SO₂ raw gas from sulphur. Values are average of numbers for single absorption and double absorption contact processes.

⁷ Balancing value based on the data from this source. Calculated with the values presented for sulphur burning, pyrites roasting, smelter gas burning and spent acid regeneration. Partial contribution of each process: 50%, 8.5%, 35% and 5.5%, respectively, in concordance with the rest of the present study. (See section 1.4)

⁸ For a conversion rate of 99%.

¹⁰ Average of values of two Austrian double contact plants for elemental sulphur burning with conversion rates of 99.7 to 99.8%.

¹¹ Average of values of two Austrian sulphuric acid plants with conversion rates of 99.7 to 99.8%.

¹⁴ CORINAIR (1992) CORINAIR-Emission Factor Handbook, part 1.: Default Emissions Factors from stationary sources. CITEPA (ed).

¹⁵ Bol, B. and Kohnen E.A. (1993) Produktie van Zwavelzuur; RIVM-report 736301143; RIZA report 92.003/43. Maart.

¹⁶ Ms Froste, Mr Kvist ans Ms Haclund. Swedish EPA. Personal communication on february 1995.

Davis (1999) quotes UNEP (1998) and consequently, these values are not presented in the table.

Regarding emissions to air, there are no significative differences between the numbers from the different sources. For SO₂ all the values are of the same magnitud order. Slight differences can be explained with the different technologies considered. In regard to SO₃, the values from ESA-EFMA (2000) and Wiesenberger (2001) are lower than the others, presumably because the first source consideres the state-of-the-art technology in Europe and the second, two modern plants in Austria. The value from Habersatter *et al.* (1998) for SO₃ seems too high and consequently is not taken into consideration.

For all the emissions the highest values available are taken, following a conservative criterion.

The values for emissions into water of sulphuric acid and sulphates are added and reported together as sulphate. The numbers for emissions to air of SO₂ and SO₃ are also reported together, as SO₂, making the necessary conversions. The emission into air of Sulfate is reported separately. The emission of SO₃ + H₂SO₄ is not considered in order to avoid overlappings with the two outputs mentioned before.

It is considered that the particulates correspond to the fraction Particulates, < 2.5 um, according to Berdowski *et al.* (2002) and assuming that this emission corresponds only to the burning of diesel fuel.

83.5.6 Wastes

Solid wastes

The most relevant solid waste mentioned in literature is **spent catalysts**. According to ESA-EFMA (2000) there is an average emission of about 2.50 E-05 kg spent catalysts.kg⁻¹ 100% H₂SO₄, with values ranging from 1.00 E-05 to 4.00 E-05 kg.kg⁻¹ 100% H₂SO₄, depending on the process. According to the mentioned source, a typical composition for spent catalyst is:

- V₂O₅: min 3% w/w
- K₂O: max. 10% w/w
- P: max. 0.5% w/w
- Sn, Pb, As, Sb, Bi, Cu, Zn, Cd, Hg: 0.1% w/w

Two methods for disposing are in use for spent catalysts. One of them is the metal recovery by which the vanadium content can be reclaimed for further use. This method is commonly practiced. The second is the landfill disposal. The catalyst can be deposited directly, usually mixed with lime to neutralize residual acidity, or it can be fixed in an inert matrix prior to controlled deposit.

Wiesenberger (2001) mentions -besides spent catalysts- also the following solid wastes:

- **residues from filtration of sulphur** in the elemental sulphur burning process.
- **burning residues, fine dust and scrubbing residues** arised by pyrite roasting. These residues are contaminated with heavy metals such as lead, cadmium and arsenic. Reprocessing of roasting residues is hardly done; they are usually disposed of. Arsenic and thallium are concentrated in the fine dusts, which are disposed of after separation.
- **fine dust and scrubbing residues** generated by burning of off-gases from nonferrous metal production. Fine dusts are processed in the non-ferrous metal industry or are internally recycled to the respective smelting plants. Compounds containing mercury are separated by reactive filters or by scrubbing processes. Scrubbing residues arising from gas purification are reused in the non-ferrous metal industry or disposed of.
- **fine dust and scrubbing residues** are produced also when using regenerative exhaust gas cleaning for the production of SO₂ and H₂SO₄. These residues are disposed of.

- **coke, ashes and slags** produced when using waste acid or metal sulphates as raw materials. Coke is recycled in the process. Depending on the composition of the waste acid, ashes and slag could be contaminated with heavy metals. Ashes and slag are disposed of.

In accordance to the last point mentioned above, UNEP (1998) also indicates that considerable amounts of **cinder** arise when using other raw materials than elemental sulphur.

Other solid wastes of less relevance mentioned are the wastes from **packaging and lining**, but no composition or amounts produced are mentioned. Wessman (2002) mentions spent washing acids but without giving values. This source mentions also 0.001 to 0.002 kg. kg⁻¹ 100% H₂SO₄ of solid waste coming out because of the energy production. An average of this numbers is added to the average for spent catalysts mentioned above. The resulting number (1.53 E-03 kg solid waste kg⁻¹ 100% H₂SO₄) and reported as “disposal, municipal solid waste, 22.9% water, to sanitariy landfill”. Even if this might not be exactly the type of waste, it is the most appropriate among the different modules available in the database.

83.6 Data Quality Considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

Data are taken from ESA-EFMA (2000) for the items sulphur consumption, emission of sulphates to air and generation of solid wastes. The main concern regarding ESA-EFMA (2000) is that it does not mention on how many different sample points the different values given are based, if these are measures or estimations and to what period of time these correspond.

The value for sulphur consumption is reported as taken from ESA-EFMA (2000), because even if many sources present the same value, this source in particular has the best data quality score.

For consumption of water and emission of sulphates to water KCL (2002) is used. This source has for this inventory in particular quite good scores due to the fact that even if they base on data from literature, they have done crosschecking with confidential data from manufacturers. The quality scores given to this source in Ecoinvent are in concordance with their own scores for the study.

EMEP/CORINAIR (2001) is used for values on emissions of SO₂ and SO₃. This survey prepared by expert panels provide with what these experts consider the best current available information, taking into account the European situation. The disadvantage of this source is that it bases only on literature data.

Numbers for emissions to air of ammonia, hydrogen chloride and particulates are taken from Patyk (1997). This source is a complete review of the available information based itself on qualified sources but it has disadvantage that the information summarized may be quite outdated. Besides, it is based on literature and theoretical calculations on similar processes and less on direct information from sulphuric acid plants.

The value of heat-waste is based on several sources and therefore, has an average quality score that consideres the corresponding scores from the mentioned sources (ESA-EFMA (2000), Patyk (1997) and Wiesenberger (2001)). The disadvantage of this highly reliable source is that since it only reports on values from Austrian production plants, it is difficult to say how representative the data are for the whole European scenario. Additionally, this source reports on state-of-the-art techniques, it is to be expected that the data from this source are reflecting a rather better environmental performance than the European average.

Habersatter *et al.* (1998) is used for the values regarding emissions of NOx and emission into water of solids. The advantage of this inventory is that it bases on real data from a manufacturing company, even if no information about number of samples or kind of measurements is available. On the other hand, it is difficult to say how representative it is for the whole European scenario.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht *et al.* (2003b) (transport) resp. the very general module of an organic chemical plant are used. The module analysed corresponds to Europe. However, the data used for this study correspond not only to whole Europe but also to the EU or Western Europe. This lack of representativeness is reflected in the uncertainty scores.

Tab. 83.6 summarizes the input and output data as well as the uncertainties used for the production of sulphuric acid. The values are given for the production of 1 kg of 100% sulphuric acid.

Tab. 83.6 Input- / Output-data for the sulphuric acid production (expressed per kg 100% sulphuric acid produced)

Explanation	Name	Location	Unit	sulphuric acid, liquid, at plant			GeneralComment
				RER	StandardDeviations	Type	
				0 kg	%		
Resources input from Technosphere	Water, unspecified natural origin		m3	4.88E-2	1	1.23	(2.3,2.3,1.5); Data from survey in literature (KCL 2002)
	secondary sulphur, at refinery	RER	kg	2.15E-1	1	1.32	(3.1,1.1,3.5); Data from survey in literature (ESA-EFMA 2000)
	diesel, at regional storage	RER	kg	7.44E-5	1	1.34	(3.2,2.3,3.5); Data from survey in literature (Patyk 1997)
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.75E-2	1	1.34	(3.2,2.3,3.5); Data from survey in literature (Patyk 1997)
	transport, freight, rail	RER	tkm	2.35E-1	1	2.05	(4.4,na,na,na,na); Standard distances
	transport, lorry 32t	RER	tkm	3.93E-2	1	2.05	(4.4,na,na,na,na); Standard distances
	chemical plant, organics	RER	tunit	2.60E-10	1	3.96	(4.1,5.3,5.4); Estimation
	waste disposal, municipal solid waste, 22.9% water, to sanitary landfill	CH	kg	9.95E-4	1	1.32	(3.1,1.1,3.5); Data from survey in literature (ESA-EFMA 2000)
	sulphuric acid, liquid, at plant	RER	kg	1.00E+0			
air emission	Heat, waste		MJ	2.69E-1	1	1.35	(3.3,3.3,3.5); Data based on literature (Patyk 1997, ESA-EFMA 2000 and Wiesenberger 2001)
	Nitrogen oxides		kg	4.88E-4	1	1.58	(2.4,2.3,1.5); Data from survey in literature (Habersatter 1998)
	Ammonia		kg	8.45E-9	1	1.65	(3.2,3.3,3.5); Data from survey in literature (Patyk 1997)
	Sulfur dioxide		kg	5.90E-3	1	1.32	(3.2,4.3,1.5); Data from survey in literature (EMEP CORINAIR 2001)
	Sulfate		kg	4.21E-3	1	1.63	(3.1,1.1,3.5); Data from survey in literature (ESA-EFMA 2000)
	Particulates, < 2.5 um		kg	2.28E-7	1	3.12	(3.2,2.3,3.5); Data from survey in literature (Patyk 1997)
	Hydrogen chloride		kg	1.30E-9	1	1.65	(3.2,3.3,3.5); Data from survey in literature (Patyk 1997)
	Solved solids		kg	9.75E-4	1	1.58	(2.4,2.3,1.5); Data from survey in literature (Habersatter 1998)
	Suspended solids, unspecified		kg	9.75E-4	1	1.58	(2.4,2.3,1.5); Data from survey in literature (Habersatter 1998)
	Sulfate		kg	3.85E-4	1	1.57	(3.2,3.1,1.5); Data from survey in literature (KCL 2002)

83.7 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

83.8 Conclusions

An average European dataset for the production of liquid sulphuric acid by contact process for the year 2000 is established. This dataset is in accordance with the present quality guidelines of the ecoinvent project and is based on various reports covering the European industry, based on statistics from the time horizon 1990 up to 2000. The data are thus of a good quality and can be used in a very broad context.

83.9 EcoSpold Meta Information

ReferenceFunction	Name	sulphuric acid, liquid, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Inventory Includes the obtention of SO ₂ -containing gas (by means of oxidation of the sulphur containing raw materials: elemental sulphur, pyrites, other sulphide ores or spent acids). It includes also the conversion of SO ₂ to SO ₃ and the absorption of SO ₃ into solution (sulfuric acid in water) to yield Sulphuric acid.
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Schwefelsäure, flüssig, ab Werk
ReferenceFunction	Synonyms	Dipping acid // Hydrogen sulfate // Sulfuric acid // Oil of vitriol
ReferenceFunction	GeneralComment	Manufacturing process starting with sulphur-containing raw materials (elemental sulphur, pyrites, ores and spent acids) is considered, plus consumption of auxiliaries, energy, infrastructure and land use, as well as transportation of raw materials, auxiliaries and wastes. The generation of solid wastes and emissions into air and water and wastes. Transport and storage of the final product sulphuric acid are not included. No byproducts or coproducts are considered. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Wastes are assumed to be sent to landfill. Inventory refers to 1 kg 100% sulphuric acid, liquid, at plant. Since the sulphuric acid can be considered a as byproduct from the processing of sulphide ores (other than pyrites), for this study it is considered that the sulphuric acid produced by smelter gas burning is obtained "gratis". As mentioned above, this process contributes with 35% to the total producti
ReferenceFunction	CASNumber	7664-93-9
TimePeriod	StartDate	2001-12
TimePeriod	EndDate	2001-12
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	Values based on literature using data from unknown date, and reports with data from 1990 to 2000, approximately.
Geography	Text	European average values
Technology	Text	part of the sources consider the average technology used in European sulphuric acid production plants. The others consider the state-of-the-art technology in Europe.
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	see OtherPeriodText
Representativeness	Extrapolations	Transports based on standard distances of Ecoinvent. Infrastructure: proxy module used (chemical plant, organics)
Representativeness	UncertaintyAdjustments	none

83.10 References

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84 Tetrachloromethane

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Last Changes:

2004

84.1 Introduction

Tetrachloromethane (CCl_4 , CAS-No. 56-23-5) is at room temperature a heavy, non-flammable, colorless liquid with a characteristic non-irritant odor (Holbrook (2000)). It is almost not soluble in water, while it is miscible with many common organic liquids. Tetrachloromethane acts as a powerful solvent. For this inventory the functional unit is 1 kg pure liquid tetrachloromethane. The most important chemical and physical properties of tetrachloromethane used in this inventory are given here.

Synonyms for tetrachloromethane: carbon tetrachloride

Tab. 84.1 Chemical and physical properties of tetrachloromethane (according to Holbrook (2000))

Property	Unit	Value	Remarks
Molecular weight	G mol^{-1}	153.82	
Melting point	°C	-22.92	at normal pressure
Boiling point	°C	76.72	at normal pressure

84.2 Reserves and Resources of material

According to Holbrook (2000), tetrachloromethane was one of the first organic chemicals that has been produced on a large scale – starting e.g. in the United States around 1907. During a long time, the production out of carbon disulphide was the only type of industrial production. Since the 50s, the chlorination of hydrocarbons (e.g. methane) has taken more and more important parts of the production. Thus, all further discussion of resources equals to the discussion about crude oil and therefore you can refer to the Dones et al. (2004).

84.3 Use of material / product

According to Holbrook (2000), nowadays the main application of tetrachloromethane are the production of chlorofluorocarbons (CFC-11, CFC-12) as well as the use as reaction medium or intermediate. Formerly – i.e. in the first part of the 20th century – tetrachloromethane was used mainly for metal degreasing, dry-cleaning, as spotting fluid, as fire extinguisher fluid or grain fumigant.

In the end of the 80s, the US production of tetrachloromethane was in the order of 350 kt. Respective information about the worldwide or the European production volume were not available.

84.4 Systems characterization

The production process for tetrachloromethane was assessed with data from Boustead (1997). Due to the fact that this dataset is cumulated it was not possible to use the other processes modelled in ecoinvent to obtain a transparent process chain. The data was nevertheless used because it represents a high share of the European production of this type of chemicals. The transformation for the data as given in Boustead (1997) to the data format in Ecoinvent is described in detail in the methodology part of the plastics part in Hischier (2004).

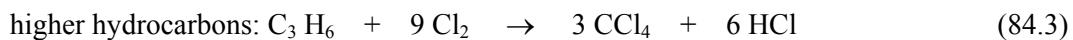
Within the module assessed here there are only the resources and emissions considered which are given in the data source. Therefore no land use could be included and no direct soil emissions within the process chain are stated. For each waste type described in the methodology used in the datasets (Boustead 1999) an appropriate waste process from the Ecoinvent modules was included.

84.5 Tetrachloromethane, at plant (Location: RER)

84.5.1 Production process

The production of tetrachloromethane according to the above mentioned process out of carbon disulphide is nowadays only used in the United States. As here, a European average module is established, this production way is not further investigated.

For the European production, three different ways can be distinguished, all of them being chlorination reactions of different hydrocarbons. Depending on the starting hydrocarbon, the following reaction equation can be established:



All these production routes can be found in Europe according to Boustead (1997) – but there is no information available how the distribution between these different processes is.

84.5.2 Inventory data

The process requirements and burdens were accounted according to the data of Boustead (1997). There was no information in those cumulated inventory data available about the used allocation method to share the burdens between the obtained products in the methane chlorination process (methyl chloride, methylene dichloride, chloroform, carbon tetrachloride). This data was nevertheless used because it represents 78% of the annual European production of chloromethanes (Boustead 1997b). In fact, the data represent 5 different European producers – producing 54 kt of tetrachloromethane.

84.5.3 Data uncertainty and input data for database ecoinvent

Tab. 84.2 and Tab. 84.3 summarize the resulting data of the average pentane production in Europe. According to the methodological remarks in Hischier (2004), these data contain no uncertainty information. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 84.9.

Tab. 84.2 Input data of the dataset "tetrachloromethane, at plant (RER)"

Explanation	Name	Location	Unit	carbon tetrachloride, at plant		UncertaintyType	StandardDeviation95%	GeneralComment	
				RER 0 kg					
		Location	InfrastructureProcess Unit						
Resources	Oil, crude, in ground		kg	1.20E-01				Uncertainty for LCI results cannot be determined	
	Gas, natural, in ground		Nm3	3.63E-01				Uncertainty for LCI results cannot be determined	
	Coal, hard, unspecified, in ground		kg	1.10E-01				Uncertainty for LCI results cannot be determined	
	Coal, brown, in ground		kg	1.80E-02				Uncertainty for LCI results cannot be determined	
	Wood, unspecified, standing		m3	7.60E-09				Uncertainty for LCI results cannot be determined	
	Energy, potential, stock, in barrage water		MJ	8.90E-01				Uncertainty for LCI results cannot be determined	
	Uranium, in ground		kg	2.19E-05				Uncertainty for LCI results cannot be determined	
	Water, cooling, unspecified natural origin		m3	1.40E-01				Uncertainty for LCI results cannot be determined	
	Water, unspecified natural origin		m3	7.50E-03				Uncertainty for LCI results cannot be determined	
	Water, river		m3	1.70E-06				Uncertainty for LCI results cannot be determined	
	Water, salt, ocean		m3	7.40E-07				Uncertainty for LCI results cannot be determined	
	Water, well, in ground		m3	1.80E-03				Uncertainty for LCI results cannot be determined	
	Barite, 15% in crude ore, in ground		kg	6.10E-04				Uncertainty for LCI results cannot be determined	
	Aluminum, 24% in bauxite, 11% in crude ore, in ground		kg	5.76E-06				Uncertainty for LCI results cannot be determined	
	Sodium chloride, in ground		kg	1.10E+00				Uncertainty for LCI results cannot be determined	
	Calcite, in ground		kg	2.20E-02				Uncertainty for LCI results cannot be determined	
	Clay, unspecified, in ground		kg	2.00E-06				Uncertainty for LCI results cannot be determined	
	Fluorspar, 92%, in ground		kg	3.00E-06				Uncertainty for LCI results cannot be determined	
	Iron, 46% in ore, 25% in crude ore, in ground		kg	8.50E-05				Uncertainty for LCI results cannot be determined	
	Sand, unspecified, in ground		kg	7.80E-04				Uncertainty for LCI results cannot be determined	
	Sulfur, in ground		kg	1.50E-03				Uncertainty for LCI results cannot be determined	
	Sylvite, 25 % in sylvinite, in ground		kg	5.00E-06				Uncertainty for LCI results cannot be determined	
Input from Technosphere	disposal, hard coal mining waste tailings, in surface backfill	GLO	kg	4.80E-02				Uncertainty for LCI results cannot be determined	
	disposal, municipal solid waste, 22.9% water, to municipal incineration	CH	kg	7.20E-03				Uncertainty for LCI results cannot be determined	
	disposal, average incineration residue, 0% water, to residual material landfill	CH	kg	2.07E-02				Uncertainty for LCI results cannot be determined	
	disposal, hazardous waste, 0% water, to underground deposit	DE	kg	4.90E-03				Uncertainty for LCI results cannot be determined	
	disposal, facilities, chemical production	RER	kg	2.00E-06				Uncertainty for LCI results cannot be determined	
	disposal, plastics, mixture, 15.3% water, to municipal incineration	CH	kg	5.00E-07				Uncertainty for LCI results cannot be determined	
	disposal, wood untreated, 20% water, to municipal incineration	CH	kg	5.00E-07				Uncertainty for LCI results cannot be determined	

Tab. 84.3 Output data of the dataset "tetrachloromethane, at plant (RER)"

Explanation	Name	Location	Unit	carbon tetrachloride, at plant		UncertaintyType	StandardDeviations95%	GeneralComment			
				RER 0 kg							
				Location	InfrastructureProcess Unit						
Output	carbon tetrachloride, at plant	RER	kg	1							
Air emission	Heat, waste		MJ	2.89E+01				Uncertainty for LCI results cannot be determined			
	Particulates, > 10 um		kg	6.72E-04				Uncertainty for LCI results cannot be determined			
	Particulates, > 2.5 um, and < 10um		kg	9.03E-04				Uncertainty for LCI results cannot be determined			
	Particulates, < 2.5 um		kg	5.25E-04				Uncertainty for LCI results cannot be determined			
	Carbon monoxide, fossil		kg	1.00E-03				Uncertainty for LCI results cannot be determined			
	Carbon dioxide, fossil		kg	1.40E+00				Uncertainty for LCI results cannot be determined			
	Sulfur dioxide		kg	7.00E-03				Uncertainty for LCI results cannot be determined			
	Nitrogen oxides		kg	7.40E-03				Uncertainty for LCI results cannot be determined			
	Dinitrogen monoxide		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	NMVOC, non-methane volatile organic compounds, unspecified origin		kg	9.69E-04				Uncertainty for LCI results cannot be determined			
	Methane, fossil		kg	9.10E-03				Uncertainty for LCI results cannot be determined			
	Hydrogen sulfide		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Hydrogen chloride		kg	6.20E-05				Uncertainty for LCI results cannot be determined			
	Chlorine		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Hydrogen fluoride		kg	3.00E-06				Uncertainty for LCI results cannot be determined			
	Lead		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Fluorine		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Halogenated hydrocarbons, chlorinated		kg	4.50E-04				Uncertainty for LCI results cannot be determined			
	Hydrocarbons, aromatic		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Aldehydes, unspecified		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Cyanide		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Sulfate		kg	4.90E-07				Uncertainty for LCI results cannot be determined			
	Hydrogen		kg	2.10E-04				Uncertainty for LCI results cannot be determined			
	Mercury		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Ammonia		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Ethane, 1,2-dichloro-		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Ethene, chloro-		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	COD, Chemical Oxygen Demand		kg	5.30E-05				Uncertainty for LCI results cannot be determined			
	BOD5, Biological Oxygen Demand		kg	1.10E-05				Uncertainty for LCI results cannot be determined			
	Acidity, unspecified		kg	1.60E-05				Uncertainty for LCI results cannot be determined			
	Solved solids		kg	1.71E-04				Uncertainty for LCI results cannot be determined			
	Ammonium, ion		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Suspended solids, unspecified		kg	1.50E-03				Uncertainty for LCI results cannot be determined			
	Phenol		kg	3.00E-06				Uncertainty for LCI results cannot be determined			
	Aluminum		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Calcium, ion		kg	2.90E-03				Uncertainty for LCI results cannot be determined			
	Copper, ion		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Iron, ion		kg	3.00E-06				Uncertainty for LCI results cannot be determined			
	Mercury		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Magnesium		kg	2.00E-06				Uncertainty for LCI results cannot be determined			
	Sodium, ion		kg	3.60E-02				Uncertainty for LCI results cannot be determined			
	Potassium, ion		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Nickel, ion		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Zinc, ion		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Nitrate		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Nitrogen		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Chloride		kg	6.30E-02				Uncertainty for LCI results cannot be determined			
	Cyanide		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Fluoride		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Sulfate		kg	1.90E-03				Uncertainty for LCI results cannot be determined			
	Carbonate		kg	5.00E-07				Uncertainty for LCI results cannot be determined			
	Phosphorus		kg	2.20E-07				Uncertainty for LCI results cannot be determined			
	Oils, unspecified		kg	1.00E-06				Uncertainty for LCI results cannot be determined			
	Chlorinated solvents, unspecified		kg	6.00E-06				Uncertainty for LCI results cannot be determined			
	Hydrocarbons, unspecified		kg	1.20E-05				Uncertainty for LCI results cannot be determined			
	Sulfide		kg	5.00E-06				Uncertainty for LCI results cannot be determined			
	TOC, Total Organic Carbon		kg	4.00E-06				Uncertainty for LCI results cannot be determined			

84.6 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

84.7 Conclusions

The inventory data used in this process does not give transparency on the processes used and allocations made due to the use of cumulated data. Therefore, many emissions especially soil emissions are not accounted. Because of the cumulated data also no land occupation and land transformation could be included in the dataset. This leads to an incompleteness of the dataset, which has to be considered when using it. Also the uncertainty of the data used could not be determined for those datasets. Never-

theless the data refers on a large share of the European production and should therefore be representative for the production of this chemical.

(See also discussion of Boustead plastic data in part II of Hischier (2004)).

84.8 References

- Boustead (1997) Boustead I. (1997) Ecoprofile of Chloromethanes. European Chlorinated Solvent Association (ECSA), Brussels
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84.9 EcoSpold Meta Information

ReferenceFunction	Name	carbon tetrachloride, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Aggregated data for all processes from raw material extraction until delivery at plant
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Tetrachlorkohlenstoff, ab Werk
ReferenceFunction	Synonyms	Tetrachloromethane
ReferenceFunction	GeneralComment	Data are from the Eco-profiles of the European plastics industry (APME). Not included are the values reported for: recyclable wastes, amount of air / N ₂ / O ₂ consumed, unspecified metal emission to air and to water, mercaptan emission to air, unspecified CFC/HCFC emission to air. The amount of "sulphur (bonded)" is assumed to be included into the amount of raw oil.
ReferenceFunction	CASNumber	56-23-5
TimePeriod	StartDate	1997
TimePeriod	EndDate	1997
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	date of literature used
Geography	Text	5 major European producers
Technology	Text	production by three different routes (methane with chlorine / chlorination of chloromethane / chlorination of higher hydrocarbons)
Representativeness	Percent	
Representativeness	ProductionVolume	unknown
Representativeness	SamplingProcedure	literature values based on company survey
Representativeness	Extrapolations	no extrapolation
Representativeness	UncertaintyAdjustments	none

85 Titanium dioxide (rutile, anatase, cosmetic white)

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 Review: Heiko Kunst, Berlin

85.1 Introduction

This chapter describes the production of titanium dioxide. This chemical is used as a whitening agent in myriad applications, from paints to toothpaste. It is also known as rutile, anatase, brookite, cosmetic white, tipaque and others.

85.2 Reserves and resources of titanium dioxide

Titanium dioxide is an inorganic chemical compound. Titanium dioxide is manufactured by processing naturally occurring the titanium-containing rutile or ilmenite minerals. Rutile is an impure form of titanium dioxide and ilmenite contains titanium combined with iron as a compound oxide. These minerals are exploited in Australia, USA, India and South Africa. (Chemlink.com)

85.3 Characterisation of titanium dioxide and its precursors

85.3.1 Titanium dioxide

Titanium dioxide is available as a white powder. Its chemical formula is TiO_2 . It is stable and non-toxic. Titanium dioxide exists in natural minerals (rutile).

Tab. 85.1 Physical properties of titanium dioxide

Molecular weight	79.9 g / mol
Boiling point	2500 – 3000 °C
Melting point	1830 -1850°C
Specific gravity	3.9 g/cm3

TiO_2 pigment is characterized by its purity, refractive index, particle size, and surface properties. The superiority of TiO_2 as a white pigment is due mainly to its high refractive index and resulting light-scattering ability, which give excellent hiding power and brightness (USGS 2003)

85.3.2 Ilmenite and rutile

Ilmenite is a black sand or rock with the formula FeTiO_3 . The TiO_2 content varies from 45%- 60%, depending on its source. Rutile is a brown to reddish-black mineral containing 95% TiO_2 . (Tioxide, 1999).

85.3.3 Titanium slag and beneficiated ilmenite

Titanium slag is the residue left after the extraction of iron from ilmenite. The use of slag as the input for TiO_2 production can reduce the use of concentrated sulphuric acid and result in less by-product iron sulfate

Beneficiated ilmenite is ilmenite which has been treated by physical or chemical means.

85.4 Production and use of titanium dioxide

In 2001, total world demand for titanium dioxide was in the order of 3.7 million tonnes. European demand was 1.15 million tonnes (industry sources).

Tab. 85.2 2001 uses of titanium dioxide (industry sources)

Uses	World	Europe
Coatings	56%	55%
Plastics	23%	22%
Paper and laminates	13%	14%
Inks	3%	2%
Others	5%	7%

Major producers include Huntsman, DuPont and Millenium Inorganics as well as Kerr-McGee..

85.5 System characterization

There are two different production processes. The sulfate process uses ilmenite and titanium slag. The chloride process uses mineral rutile and beneficiated ilmenite as well as titanium slag. (Tioxide, 1999).

85.5.1 Ilmenite and rutile sourcing

Ilmenite and rutile are produced: from heavy-mineral sands dredging operations.(open-cast or dredge mining).

85.5.2 Sulfate process (UBA BAT Notes, 2001)

Ilmenite or titanium slag are dried and ground. Concentrated sulphuric acid is then added. The hydration heat and the formation of sulfate leads to a temperature rise to 170 – 220 °C. (1)



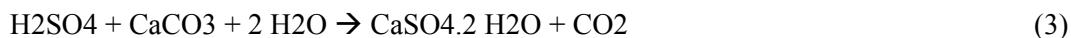
The resulting cake is dissolved in water. All insoluble materials are separated and centrifuging or filtration can remove the iron sulfate. The resulting material is known as copperas. It can be used in wastewater treatment or it can be roasted and thermally decomposed to Fe_2O_3 and SO_2 . Titanium oxide hydrate is precipitated by hydrolysis and steam addition (2).



The hydrate is separated by filtration from the spent acid. The hydrate is washed with water or weak acid, after which it still contains some acid. For the production of pure technical grade product, it is calcined. Sulfur trioxide is separated, which is decomposed to SO_2 and oxygen. After calcinations, the product is slowly cooled, which prevents the formation of trivalent titanium, which would have an undesired effect on the color. Most pigment is wet milled and further treated with inorganic oxides to coat the titanium oxide particles (this step is not included in the developed inventories below).

The spent sulphuric acid contains large amounts of iron sulfate. Total volume of spent acid per ton of product is 6- 9 tons. The spent acid used to be simply discharged to sea in the 1980's and early 1990's e.g. by a German producer to the North Sea), which gave the product some notoriety. However, the acid is now often reconcentrated and sold or reused in the process. Some sites continue to discharge sulphuric acid to sea. The residual iron oxide can be used in the cement industry.

Neutralisation is carried out by the addition of calcium carbonate (soda) to give white gypsum



The white gypsum can be sold for use in plasterboard or cement. The CO₂ can be captured and sold.

Further neutralisation can be carried out by using calcium hydroxide:



This gypsum also contains the remaining iron from the ore as ferrous hydroxide. It will oxidize to ferrous oxide, giving the gypsum a reddish color. Red gypsum can be sold to improve agricultural soil. (Tioxide 1999)

85.5.3 Production of synthetic rutile for the chloride process

The Austpac Enhanced Roasting and Magnetic Separation (ERMS) is a roasting process, which magnetises ilmenite and allows it to be leached in hydrochloric acid. Magnetised ilmenite can then be easily separated from minerals such as chromite.

Ilmenite can be ERMS roasted to convert the titanium component into the insoluble rutile form. It can then be leached at atmospheric pressure in strong hydrochloric acid to remove the iron, leaving a network of rutile crystals. This synthetic rutile is then washed, filtered and heated (calcined) to make the final saleable product. The iron chloride liquors are then processed to regenerate the strong acid, leaving iron oxide pellets that can be sold to a steel plant or disposed of as inert landfill.

85.5.4 Chloride process (UBA BAT Notes, 2001)

The newer chloride process avoids the iron sulfate waste problem. It requires the ilmenite to be processed to the rutile form (i.e. removal of the iron component to yield crude titanium dioxide, also known as synthetic rutile. (see above).

The chlorination of the raw materials slag, rutile, synthetic rutile takes place in a reactor with coke as a reducing agent. This produces titanium tetrachloride in vapor form. The TiCl₄ is distilled, then oxidized. (4), (5)





The major share of the chlorine is emitted during combustion and is recycled back to the process. Some chlorine is converted to HCl, but most (upwards of 98%) is recycled. The chlorination temperature is about 1000 °C. TiCl₄ is separated and the residual off-gases are treated. The liquid TiCl₄ is combusted to TiO₂. Combustion temperatures range from about 900 – 2000 °C. The hot off-gases are cooled and the TiO₂ is separated by filtering. the off-gases are recycled to the combustion chanber.

Also obtained is a metal chloride solution that contains mostly iron (II). Under certain conditions this solution can be used as a precipitation agent, otherwise it is treated with lime and the solids are land-filled. The calcium chloride is an effluent resulting from lime treatment and can be drained to sea (Chemlink.com).

85.6 Life cycle Inventory for titanium dioxide

This inventory is based on confidential information provided by industry sources. The input information may not be divulged. Some data can be compared with minimum and maximum values of all German production locations (UBA BAT Notes, 2001).

85.6.1 Precursor materials

Tab. 85.3 precursors for TiO₂ production

Kg per kg of product	Sulfate process	Chloride process	Source
Sulphuric acid	2.4 – 3.5		(UBA BAT Notes, 2001)
Rutile, ilmenite	Ca. 2	na	Industry sources
Synthetic rutile	ng	1.06	(Chemlink.com)
Chlorine	na	0.18	(UBA BAT Notes, 2001)

This report assumes that the sulfate process titanium dioxide has been manufactured from ilmenite, although in fact titanium slag is also used. The chloride process titanium dioxide is also assumed to stem from ilmenite, although in fact rutile, synthetic rutile and /or beneficiate are used. The data for mining of ilmenite are taken from (BUWAL 232). Transports are assumed to be from Capetown and from Melbourne to Rotterdam with some 200 km trucking in Europe.

85.6.2 Energy usage

Tab. 85.4 energy consumption for TiO₂ production (sulfate process) (UBA BAT Notes, 2001)

Consumption per kg of product (MJ/kg)	TiO ₂ manufacture	Follow-up treatment	Acid concentration and filter salt decomposition	Total
Electric energy	1.5 – 2.31	0.6 – 1.46	0.13-1.3	
Steam	3.7 – 7.7	6.7 – 10.47	0 – 6.07	
Gas	7.3 – 11.85	2.37 – 4.22	0 – 0.1	
Coal	na	na	5.8 – 8.5	
Total	12.6 – 20.5	9.9 – 14.3	5.9 – 15.2	32.7 – 40.9

Note: values can vary, depending on whether or not acid is reconcentrated or neutralized. Both steam and electricity can be generated from combined heat and power plants (CHP's). Steam can stem from sulphuric acid plants (steam burning). Electricity can stem from the grid. The model facility portrayed in this report uses power and steam from a CHP plant as well as electricity from the UCTE grid. It is furthermore assumed that acid is reconcentrated and reused. The filter salts that are produced can be sold.

Tab. 85.5 energy consumption for TiO₂ production (chloride process) (UBA BAT Notes, 2001)

Consumption per kg of product (MJ/kg)	TiO ₂ manufacture	Follow-up treatment	Total
Electric energy	1.51	0.83	
Steam	1.7	7.7	
Gas	2.9	4.2	
Total	6.1	12.7	18.8

The model facility portrayed here uses natural gas in a boiler to produce steam and imports UCTE grid electricity.

85.6.3 Air emissions

Tab. 85.6 direct air emissions for TiO₂ production (sulfate process) (UBA BAT Notes, 2001)

Gram per kg of product	Storage / grinding/drying	Decomposition	Calcination	Follow-up treatment
Particles	0.001 – 0.04	ng	0.13-1.3 *	0.002 – 0.12
NO _x	0.001 – 0.043	ng	0 – 6.07	
SO ₂	ng	0 – 0.119	1*	ng
H ₂ S	ng	0 – 0.005	ng	ng

* 0.7 g / kg is used in this report

** This value is used for the model sulfate plant.

Tab. 85.7 direct air emissions for TiO₂ production (chloride process) (UBA BAT Notes, 2001)

Gram per kg of product	Storage	Solids treatment	Off-gas treatment	Follow-up treatment
Particles	0.005	ng	ng	0.186
HCl	ng	0.007	0.024 *	ng
SO ₂	ng	ng	1.68	ng

* This value is used for the model chloride plant.

85.6.4 Wastewater emissions

Tab. 85.8 wastewater emissions for TiO₂ production (sulfate process) (UBA BAT Notes, 2001)

Gram per kg of product	Filtration / washing	Follow-up treatment
Sulfate	30 – 300 *	80 - 110
Iron	0.25 – 5 **	ng
Cadmium	0.000001	ng
Mercury	0.00000032	ng

* This report uses a value of 150 g sulfate per kg produced TiO₂

**This report uses a value of 2 g iron per kg produced TiO₂

Tab. 85.9 wastewater emissions for TiO₂ production (chloride process) (UBA BAT Notes, 2001)

Gram per kg of product	Preparation of the separated solids	Follow-up treatment
Iron	0.011 *	ng
Cadmium	0.00000022	ng
Mercury	0.00000022	ng
Filter residues	0.11	2.25

This report uses a value of 0.5 g iron per kg produced TiO₂

85.6.5 Liquid wastes

According to (UBA BAT Notes, 2001) Figure 2.1.3.1, sulphuric acid that enters the wastewater from the sulfate process contains 30 – 300 g sulfate per kg spent acid (see Tab. 85.9). An average of roughly 50 g sulfate / kg product is assumed in this report.

85.6.6 Solid wastes (UBA BAT Notes, 2001)

Sulfate process: According to (UBA BAT Notes, 2001), residues generated from ore digestion total 340 – 670 g / kg product. These wastes are disposal of as hazardous wastes.. If the acid is neutralized with lime or calcium carbonate, gypsum (calcium sulfate) can be generated in large quantities. Gypsum can be sold for use in the plasterboard, cement and paper industry, demand is growing. This report assumes that 480 g / kg product are produced, solidified in cement and landfilled.

Chloride process. According to (UBA BAT Notes, 2001), chloride process sludges total 184 g / kg product. Industry sources however suggest somewhat higher values, ranging up to 1 kg / kg product

(depending on water content). The wastes are considered to be non-hazardous. This report assumes that 960 g / kg product are landfilled (water content > 50% by weight).

85.6.7 Co-products

Sulfate process: When the spent sulphuric acid is reconcentrated and reused or sold, a variety of iron salts can be sold. These may include copperas, ferric sulfate and filter salts. If the sulphuric acid is neutralized, large amounts of gypsum may be produced, some of which can be sold on the market. None of the current price ranges allow for an allocation of the processes to these co-products, as the price x mass does not exceed the 5% cut-off considered to be the minimum for products.

85.6.8 Infrastructure

No information is given.

85.7 Data quality considerations

The data quality is considered to be fair. The inputs of raw materials are approximate, and the emissions are incomplete. The inventory is based on a mix of the sulfate and chloride processes that is somewhat representative of worldwide production. .

85.8 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

85.9 References

USGS 2003	http://minerals.er.usgs.gov/minerals/pubs/commodity/titanium/ .
Chemlink.com	http://www.chemlink.com.au/titanium.htm
Tioxide 1999	Tioxide Group: "Manufacture and General Properties of Titanium Dioxide Pigments", October 1999
UBA BAT Notes, 2001	UBA, German federal Environmental Agency: "German Notes on BAT for the production of Large Volume solid inorganic Chemicals – Titanium dioxide", June 2001
BUWAL 232	BUWAL (Swiss EPA), Environmental Series 232, "Comparative Environmental Assessment of Construction Paints and Coatings", 1995

86 Toluene

Author: Mike Chudacoff, Chudacoff Oekoscience, Zurich
 Roland Hischier, Empa, St. Gallen (Changes 2007)

Review: Heiko Kunst, TU Berlin

Last Changes: 2007

86.1 Introduction

This chapter describes the production of toluene. This chemical is used primarily for the further production of benzene, apart from its use in gasoline to increase the octane number.

Synonyms for toluene: toluol, methylbenzene, phenylmethane

86.2 Reserves and resources of toluene

Toluene is an organic chemical compound. It is produced from catalytic reforming of petroleum.

86.3 Characterisation of toluene

Toluene is a colorless liquid that is highly flammable. The vapors are heavier than air and can travel longer distances to an ignition source and then flash back. Toluene is soluble in benzene, ethyl alcohol, ketones and most organic solvents, but hardly soluble in water. Melting point -95°C, boiling point 110.6 °C. Leakage of toluene into soil or water is considered a major pollution incident (Wells (1999)). Inhalation may cause anaesthetic effects, aspiration may result in severe lung damage.

86.4 Production and use of toluene

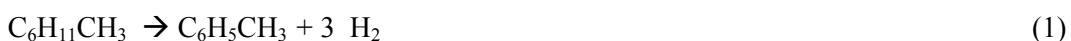
According to European Commission (2002), half of all toluene produced in Europe stems from pyrolysis gasoline and reformat, while in the U.S., 85% stems from reformat.

Over half of toluene production is used for benzene production by dealkylating the toluene. Another major use of toluene is the production of phenol, which in turn is used as a precursor of caprolactam, a building block for nylons, synthetic fibers and resins. About 12 % of toluene production goes into the prouction of toluene diisocyanate, which goes into polyurethane foams (European Commission (2002)).

In 1997-2000, European production of toluene was approximately 2.7 million tons, according to European Commission (2002). Major plants are operated in Germany, the Netherlands, Italy, Spain, the UK, the US, Japan, Taiwan, South Korea, among others. Major manufacturers include Exxon Chemical, ICI, and BP Chemicals.

86.5 System characterization

This report assumes that toluene is produced industrially from catalytic reforming of petroleum. This process passes an aromatic-rich hydrocarbon mixture over a dehydrogenation catalyst. After cooling, the reaction gases are compressed and hydrogen that is produced by the reforming reaction is recycled – overall yield: 85-90% (Wells (1999)).



86.5.1 Precursor materials (European Commission (2002))

Up to 0.3 tons of toluene can be produced per ton of reformat. Usually, all or part of the toluene is transformed into benzene or mixed xylenes.

86.5.2 Energy usage

Tab. 86.1 Energy usage for toluene production (European Commission (2002))

Consumption per ton of feedstock	Reformate plant
Fuel gas	3 – 10 kg
Steam (tons)	0.5 – 1.5
Electricity (MWh)	<0.07
Production (tons) per ton of feedstock	
Benzene	0.12 – 0.24
Toluene	0 – 0.3

86.5.3 Air emissions

Little is given on toluene production alone as most information pertains to benzene or BTX production plants.

Tab. 86.2 Air emissions for toluene production (European Commission (2002))

Air pollutant (kg/ton product)	NOx	SO2	Particulates	VOC *	Methane
BTX from aromatic mixture (source: a single plant)	0.86	0.53	0.008 kg/ton feedstock	0.03 toluene 0.2 NMVOCtot*	0.09
Benzene from pyrolysis gas (source: a single plant)	0.013	0	0.0025 kg/ton feedstock	0.03**NMVOCtot	ng

* tanks and various fugitive sources, calculated according to table 8.9 (IPPC Chemicals, 1992)

** benzene: 0.010, toluene: 0.004, pentanes 0.004

Most VOC emissions are normally fugitive (valves, flanges) and from maintenance or inspections. They may also stem from small leaks in cooling systems as well as storage tank breathing losses and displacement.

86.5.4 Wastewater emissions

BTX production entails little or no continuous wastewater. The main source is process water or condensates of distillation towers that may contain small amounts of dissolved organics. The water is treated in a facility WWTP. There also may be some wastewater containing sulfides or COD.

Tab. 86.3 Wastewater from toluene production (European Commission (2002))

Pollutant (kg/ton product)	Benzene	Toluene	COD	N-Kjeldahl	Sulfide
BTX from aromatic mixture (source: a single plant)	0.003	0.001	0.087	0.0009*	ng
Benzene from pyrolysis gas (source: a single plant)	ng	ng	ng	ng	0.075

86.5.5 Liquid wastes

No liquid wastes are given.

86.5.6 Solid wastes

The wastes are usually recycled, landfilled or incinerated in a hazardous waste incinerator. The main solid wastes are spent catalyst (from the hydrogenation process), clay from olefins removal, adsorbents from xylene separation and sludge recovered from process equipment. There are also oil-contaminated materials and sludges, which are incinerated with heat recovery. Amounts are given according to (European Commission (2002), Chapter 8.11).

Tab. 1.4 Solid wastes from BTX production (European Commission (2002))

Pollutant (kg/ton product)	Catalysts*	Clay, desiccant material, inert balls**	Activated carbon***	Filter cloth, „etc.“ ***
BTX from aromatic mixture (source: a single plant)	0.05	0.006	0.01	0.0009*
Benzene from pyrolysis gas (source: a single plant)	0.037	ng	ng	ng

* recycled via supplier

** reused after regeneration

*** incinerated

86.6 Life cycle inventory for Toluene

The production process for toluene was assessed with data from PlasticsEurope (Boustead (2005-07)), which assumes that toluene stems mostly from catalytic reforming. The data stem from the year 2002 and account for the toluene production in eleven European production sites. Due to the fact that this dataset is cumulated it was not possible to use the other processes modelled in ecoinvent to obtain a transparent process chain. The data was nevertheless used because it represents a high share of the European production of this type of chemicals. The transformation for the data as given in Boustead (2005-07) to the data format in ecoinvent is described in detail in the methodology part of the plastics part in Hischier (2007).

Within the module assessed here there are only the resources and emissions considered which are given in the data source. Therefore no land use could be included and no direct soil emissions within the process chain are stated. For each waste type used in the original dataset, an appropriate waste process from the Ecoinvent modules was included.

86.7 Data quality considerations

Tab. 86.4 and Tab. 86.6 summarize the resulting data of the toluene production in Europe. According to the methodological remarks in Hischier (2007), these data contain no uncertainty information. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 86.12.

Tab. 86.4 Input data and functional unit outflow of the dataset for toluene production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	toluene, liquid, at plant	RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment
	662	Location						
	493	InfrastructureProcess						
	403	Unit						
Resources		Oil, crude, in ground	kg	7.76E-01				Uncertainty for LCI results cannot be determined
		Gas, natural, in ground	Nm3	6.67E-01				Uncertainty for LCI results cannot be determined
		Coal, hard, unspecified, in ground	kg	4.15E-02				Uncertainty for LCI results cannot be determined
		Coal, brown, in ground	kg	2.96E-08				Uncertainty for LCI results cannot be determined
		Peat, in ground	kg	1.06E-04				Uncertainty for LCI results cannot be determined
		Wood, unspecified, standing	m3	3.32E-09				Uncertainty for LCI results cannot be determined
		Energy, potential (in hydropower reservoir), converted	MJ	5.54E-02				Uncertainty for LCI results cannot be determined
		Uranium, in ground	kg	2.40E-06				Uncertainty for LCI results cannot be determined
		Energy, gross calorific value, in biomass	MJ	8.80E-02				Uncertainty for LCI results cannot be determined
		Barite, 15% in crude ore, in ground	kg	2.85E-08				Uncertainty for LCI results cannot be determined
		Aluminium, 24% in bauxite, 11% in crude ore, in ground	kg	3.83E-07				Uncertainty for LCI results cannot be determined
		Clay, bentonite, in ground	kg	1.01E-04				Uncertainty for LCI results cannot be determined
		Anhydrite, in ground	kg	1.00E-05				Uncertainty for LCI results cannot be determined
		Calcite, in ground	kg	3.44E-04				Uncertainty for LCI results cannot be determined
		Clay, unspecified, in ground	kg	2.77E-10				Uncertainty for LCI results cannot be determined
		Chromium, 25.5% in chromite, 11.6% in crude ore, in ground	kg	1.33E-12				Uncertainty for LCI results cannot be determined
		Copper, 0.99% in sulfide, Cu 0.36% and Mo 8.2E-3% in crude ore, in ground	kg	7.96E-09				Uncertainty for LCI results cannot be determined
		Dolomite, in ground	kg	4.25E-06				Uncertainty for LCI results cannot be determined
		Iron, 46% in ore, 25% in crude ore, in ground	kg	3.46E-04				Uncertainty for LCI results cannot be determined
		Feldspar, in ground	kg	3.00E-16				Uncertainty for LCI results cannot be determined
		Manganese, 35.7% in sedimentary deposit, 14.2% in crude ore, in ground	kg	4.46E-07				Uncertainty for LCI results cannot be determined
		Fluorspar, 92%, in ground	kg	1.87E-07				Uncertainty for LCI results cannot be determined
		Granite, in ground	kg	1.57E-15				Uncertainty for LCI results cannot be determined
		Gravel, in ground	kg	1.28E-06				Uncertainty for LCI results cannot be determined
		Cinnabar, in ground	kg	7.12E-10				Uncertainty for LCI results cannot be determined
		Magnesite, 60% in crude ore, in ground	kg	1.86E-18				Uncertainty for LCI results cannot be determined
		Nickel, 1.98% in silicates, 1.04% in crude ore, in ground	kg	7.32E-13				Uncertainty for LCI results cannot be determined
		Olivine, in ground	kg	3.24E-06				Uncertainty for LCI results cannot be determined
		Lead, 5.0% in sulfide, Pb 3.0%, Zn, Ag, Cd, In, in ground	kg	1.72E-07				Uncertainty for LCI results cannot be determined
		Phosphorus, 18% in apatite, 12% in crude ore, in ground	kg	1.32E-12				Uncertainty for LCI results cannot be determined
		Sylvite, 25 % in sylvite, in ground	kg	5.95E-09				Uncertainty for LCI results cannot be determined
		TiO2, 95% in rutile, 0.40% in crude ore, in ground	kg	3.92E-34				Uncertainty for LCI results cannot be determined
		Sulfur, in ground	kg	7.76E-05				Uncertainty for LCI results cannot be determined
		Sand, unspecified, in ground	kg	6.81E-05				Uncertainty for LCI results cannot be determined
		Shale, in ground	kg	2.84E-05				Uncertainty for LCI results cannot be determined
		Sodium chloride, in ground	kg	4.27E-04				Uncertainty for LCI results cannot be determined
		sodium nitrate, in ground	kg	5.58E-18				Uncertainty for LCI results cannot be determined
		Talc, in ground	kg	9.02E-28				Uncertainty for LCI results cannot be determined
		Zinc, 9.0% in sulfide, Zn 5.3%, Pb, Ag, Cd, In, in ground	kg	6.30E-09				Uncertainty for LCI results cannot be determined
		Water, unspecified natural origin	m3	8.20E-04				Uncertainty for LCI results cannot be determined
		Water, river	m3	2.01E-04				Uncertainty for LCI results cannot be determined
		Water, salt, ocean	m3	5.92E-04				Uncertainty for LCI results cannot be determined
		Water, well, in ground	m3	8.50E-11				Uncertainty for LCI results cannot be determined
		Water, cooling, unspecified natural origin	m3	8.99E-02				Uncertainty for LCI results cannot be determined
Input from Technosphere		disposal, facilities, chemical production	kg	1.93E-05				Uncertainty for LCI results cannot be determined
		disposal, hard coal mining waste tailings, in surface backfill	kg	8.46E-03				Uncertainty for LCI results cannot be determined
		disposal, municipal solid waste, 22.9% water, to municipal incineration	kg	1.47E-03				Uncertainty for LCI results cannot be determined
		disposal, average incineration residue, 0% water, to residual material landfill	kg	3.69E-03				Uncertainty for LCI results cannot be determined
		disposal, wood untreated, 20% water, to municipal incineration	kg	4.36E-08				Uncertainty for LCI results cannot be determined
		disposal, plastics, mixture, 15.3% water, to municipal incineration	kg	2.16E-06				Uncertainty for LCI results cannot be determined
		disposal, hazardous waste, 0% water, to underground deposit	kg	1.68E-03				Uncertainty for LCI results cannot be determined
Output		toluene, liquid, at plant	kg	1.00E+00				

Tab. 86.5 Emission to air data for toluene production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	toluene, liquid, at plant	RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment
		662	Location					
Air emission	403	493	InfrastructureProcess	Unit	RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment
		Heat, waste	MJ	1.77E+01				Uncertainty for LCI results cannot be determined
		Particulates, > 10 um	kg	1.26E-04				Uncertainty for LCI results cannot be determined
		Particulates, > 2.5 um, and < 10um	kg	1.70E-04				Uncertainty for LCI results cannot be determined
		Particulates, < 2.5 um	kg	9.88E-05				Uncertainty for LCI results cannot be determined
		Carbon monoxide, fossil	kg	2.04E-03				Uncertainty for LCI results cannot be determined
		Carbon monoxide, biogenic	kg	3.62E-06				Uncertainty for LCI results cannot be determined
		Carbon dioxide, fossil	kg	1.18E+00				Uncertainty for LCI results cannot be determined
		Carbon dioxide, biogenic	kg	2.10E-03				Uncertainty for LCI results cannot be determined
		Sulfur dioxide	kg	2.28E-03				Uncertainty for LCI results cannot be determined
		Hydrogen sulfide	kg	1.16E-08				Uncertainty for LCI results cannot be determined
		Nitrogen oxides	kg	2.06E-03				Uncertainty for LCI results cannot be determined
		Ammonia	kg	1.13E-10				Uncertainty for LCI results cannot be determined
		Chlorine	kg	2.13E-10				Uncertainty for LCI results cannot be determined
		Hydrogen chloride	kg	2.11E-05				Uncertainty for LCI results cannot be determined
		Fluorine	kg	2.70E-11				Uncertainty for LCI results cannot be determined
		Hydrogen fluoride	kg	7.91E-07				Uncertainty for LCI results cannot be determined
		NMVOC, non-methane volatile organic compounds, unspecified origin	kg	1.88E-03				Uncertainty for LCI results cannot be determined
		Aldehydes, unspecified	kg	4.96E-16				Uncertainty for LCI results cannot be determined
		Lead	kg	4.49E-10				Uncertainty for LCI results cannot be determined
		Mercury	kg	9.12E-10				Uncertainty for LCI results cannot be determined
		Sulfate	kg	3.57E-15				Uncertainty for LCI results cannot be determined
		Dinitrogen monoxide	kg	5.15E-11				Uncertainty for LCI results cannot be determined
		Hydrogen	kg	2.15E-05				Uncertainty for LCI results cannot be determined
		Ethane, 1,2-dichloro-	kg	8.47E-12				Uncertainty for LCI results cannot be determined
		Ethene, chloro-	kg	1.68E-10				Uncertainty for LCI results cannot be determined
		Halogenated hydrocarbons, chlorinated	kg	4.97E-09				Uncertainty for LCI results cannot be determined
		Cyanide	kg	2.39E-18				Uncertainty for LCI results cannot be determined
		Methane, fossil	kg	1.23E-02				Uncertainty for LCI results cannot be determined
		Methane, biogenic	kg	2.18E-05				Uncertainty for LCI results cannot be determined
		Hydrocarbons, aromatic	kg	1.30E-05				Uncertainty for LCI results cannot be determined
		Hydrocarbons, aliphatic, alkanes, cyclic	kg	2.56E-06				Uncertainty for LCI results cannot be determined
		Carbon disulfide	kg	7.38E-11				Uncertainty for LCI results cannot be determined
		Methane, dichloro-, HCC-30	kg	5.07E-13				Uncertainty for LCI results cannot be determined
		Copper	kg	1.20E-11				Uncertainty for LCI results cannot be determined
		Arsenic	kg	5.29E-11				Uncertainty for LCI results cannot be determined
		Cadmium	kg	1.16E-11				Uncertainty for LCI results cannot be determined
		Silver	kg	4.31E-14				Uncertainty for LCI results cannot be determined
		Zinc	kg	3.98E-11				Uncertainty for LCI results cannot be determined
		Chromium	kg	1.41E-06				Uncertainty for LCI results cannot be determined
		Selenium	kg	1.49E-15				Uncertainty for LCI results cannot be determined
		Nickel	kg	2.56E-06				Uncertainty for LCI results cannot be determined
		Antimony	kg	1.77E-15				Uncertainty for LCI results cannot be determined
		Ethene	kg	2.42E-06				Uncertainty for LCI results cannot be determined
		Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin	kg	1.27E-31				Uncertainty for LCI results cannot be determined
		Benzene	kg	2.89E-06				Uncertainty for LCI results cannot be determined
		Toluene	kg	4.53E-07				Uncertainty for LCI results cannot be determined
		Xylene	kg	3.22E-07				Uncertainty for LCI results cannot be determined
		Benzene, ethyl-	kg	1.94E-07				Uncertainty for LCI results cannot be determined
		Styrene	kg	3.76E-10				Uncertainty for LCI results cannot be determined
		Propene	kg	1.79E-06				Uncertainty for LCI results cannot be determined

Tab. 86.6 Emission to air data for toluene production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	toluene, liquid, at plant	RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment
Water emission	662	Location						
	493	Infrastructure						
	403	Process						
		Unit						
	COD, Chemical Oxygen Demand		kg	2.59E-04				Uncertainty for LCI results cannot be determined
	BOD5, Biological Oxygen Demand		kg	6.13E-05				Uncertainty for LCI results cannot be determined
	Lead		kg	2.46E-10				Uncertainty for LCI results cannot be determined
	Iron, ion		kg	1.48E-08				Uncertainty for LCI results cannot be determined
	Sodium, ion		kg	1.22E-04				Uncertainty for LCI results cannot be determined
	Acidity, unspecified		kg	9.29E-07				Uncertainty for LCI results cannot be determined
	Nitrate		kg	4.93E-06				Uncertainty for LCI results cannot be determined
	Mercury		kg	1.22E-10				Uncertainty for LCI results cannot be determined
	Ammonium, ion		kg	1.78E-06				Uncertainty for LCI results cannot be determined
	Chloride		kg	7.30E-05				Uncertainty for LCI results cannot be determined
	Cyanide		kg	3.28E-11				Uncertainty for LCI results cannot be determined
	Fluoride		kg	1.33E-09				Uncertainty for LCI results cannot be determined
	Sulfide		kg	7.88E-12				Uncertainty for LCI results cannot be determined
	Hydrocarbons, unspecified		kg	1.78E-05				Uncertainty for LCI results cannot be determined
	Suspended solids, unspecified		kg	7.95E-05				Uncertainty for LCI results cannot be determined
	Oils, unspecified		kg	3.56E-05				Uncertainty for LCI results cannot be determined
	Chlorinated solvents, unspecified		kg	5.69E-09				Uncertainty for LCI results cannot be determined
	Chlorine		kg	1.26E-09				Uncertainty for LCI results cannot be determined
	Phenol		kg	5.11E-07				Uncertainty for LCI results cannot be determined
	Solved solids		kg	1.29E-05				Uncertainty for LCI results cannot be determined
	Phosphorus		kg	5.69E-08				Uncertainty for LCI results cannot be determined
	Nitrogen		kg	2.93E-06				Uncertainty for LCI results cannot be determined
	Sulfate		kg	3.71E-04				Uncertainty for LCI results cannot be determined
	Ethane, 1,2-dichloro-		kg	1.86E-13				Uncertainty for LCI results cannot be determined
	Ethene, chloro-		kg	3.12E-12				Uncertainty for LCI results cannot be determined
	Potassium, ion		kg	1.76E-10				Uncertainty for LCI results cannot be determined
	Calcium, ion		kg	3.12E-08				Uncertainty for LCI results cannot be determined
	Magnesium		kg	5.68E-10				Uncertainty for LCI results cannot be determined
	Chromium, ion		kg	1.35E-12				Uncertainty for LCI results cannot be determined
	Chlorate		kg	9.92E-08				Uncertainty for LCI results cannot be determined
	Bromate		kg	6.50E-10				Uncertainty for LCI results cannot be determined
	TOC, Total Organic Carbon		kg	3.79E-05				Uncertainty for LCI results cannot be determined
	AOX, Adsorbable Organic Halogen as Cl		kg	5.77E-13				Uncertainty for LCI results cannot be determined
	Aluminum		kg	1.28E-06				Uncertainty for LCI results cannot be determined
	Zinc, ion		kg	3.44E-08				Uncertainty for LCI results cannot be determined
	Copper, ion		kg	1.96E-08				Uncertainty for LCI results cannot be determined
	Nickel, ion		kg	4.59E-10				Uncertainty for LCI results cannot be determined
	Carbonate		kg	1.30E-04				Uncertainty for LCI results cannot be determined
	Arsenic, ion		kg	6.00E-10				Uncertainty for LCI results cannot be determined
	Cadmium, ion		kg	4.22E-15				Uncertainty for LCI results cannot be determined
	Manganese		kg	1.73E-14				Uncertainty for LCI results cannot be determined
	Tin, ion		kg	2.31E-16				Uncertainty for LCI results cannot be determined
	Strontium		kg	1.04E-11				Uncertainty for LCI results cannot be determined
	Silicon		kg	1.49E-19				Uncertainty for LCI results cannot be determined
	Benzene		kg	1.20E-10				Uncertainty for LCI results cannot be determined
	Molybdenum		kg	-				Uncertainty for LCI results cannot be determined

86.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

86.9 Conclusions

The inventory data used in this process does not give transparency on the processes used and allocations made due to the use of cumulated data. Therefore, many emissions especially soil emissions are not accounted. Because of the cumulated data also no land occupation and land transformation could be included in the dataset. This leads to an incompleteness of the dataset, which has to be considered when using it. Also the uncertainty of the data used could not be determined for those datasets. Nevertheless the data refers on a large share of the European production and should therefore be representative for the production of this chemical.

86.10EcoSpold Meta Information

ReferenceFunction	401 Name	toluene, liquid, at plant
Geography	662 Location	RER
ReferenceFunction	493 InfrastructureProcess	0
ReferenceFunction	403 Unit	kg
ReferenceFunction	402 IncludedProcesses	Aggregated data for all processes from raw material extraction until delivery at plant
ReferenceFunction	404 Amount	1
ReferenceFunction	490 LocalName	Toluol, flüssig, ab Werk
ReferenceFunction	491 Synonyms	
ReferenceFunction	492 GeneralComment	Data are from the Eco-profiles of the European plastics industry (PlasticsEurope). Not included are the values reported for: recyclable wastes, amount of air / N ₂ / O ₂ consumed, unspecified metal emission to air and to water, mercaptan emission to air, unspecified CFC/HCFC emission to air, dioxin to water. The amount of "sulphur (bonded)" is assumed to be included into the amount of raw oil.
ReferenceFunction	502 CASNumber	108-88-3
TimePeriod	601 StartDate	2001
TimePeriod	602 EndDate	2002
TimePeriod	603 DataValidForEntirePeriod	1
TimePeriod	611 OtherPeriodText	time to which data refer
Geography	663 Text	11 European plants
Technology	692 Text	production by catalytic reforming out of naphtha
Representativeness	722 Percent	
Representativeness	724 ProductionVolume	2.7 Mt in Europe in 2000
Representativeness	725 SamplingProcedure	literature values based on company survey
Representativeness	726 Extrapolations	no extrapolation
Representativeness	727 UncertaintyAdjustments	none

86.11 References

- Boustead (2005-07) Boustead I. (2005-07) Electronic documents with the datasets from the PlasticsEurope Eco-Profiles - Calculation results from March 2005. Download of December 18 from <http://www.plasticseurope.org>.
- European Commission (2002) European Commission (2002) Integrated Pollution Prevention and Control (IPPC) - Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry. Institute for Prospective Technological Studies, Sevilla
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- Wells (1999) Wells M. G. (1999) Handbook of Petrochemicals and Processes, 2nd Edition. Gower Publishing Company Ltd., Ashgate (United Kingdom)

86.12EcoSpold Meta Information

ReferenceFunction	Name	toluene, liquid, at plant
Geography	Location	RER
ReferenceFunction	InfrastructureProcess	0
ReferenceFunction	Unit	kg
ReferenceFunction	IncludedProcesses	Aggregated data for all processes from raw material extraction until delivery at plant
ReferenceFunction	Amount	1
ReferenceFunction	LocalName	Toluol, flüssig, ab Werk
ReferenceFunction	Synonyms	
ReferenceFunction	GeneralComment	Data are from the Eco-profiles of the European plastics industry (APME). Not included are the values reported for: recyclable wastes, amount of air / N ₂ / O ₂ consumed, unspecified metal emission to air and to water, mercaptan emission to air, unspecified CFC/HCFC emission to air. The amount of "sulphur (bonded)" is assumed to be included into the amount of raw oil.
ReferenceFunction	CASNumber	108-88-3
TimePeriod	StartDate	1990
TimePeriod	EndDate	1996
TimePeriod	DataValidForEntirePeriod	1
TimePeriod	OtherPeriodText	time to which data refer
Geography	Text	10 European plants (B, D, It, NL)
Technology	Text	production by catalytic reforming out of naphtha
Representativeness	Percent	
Representativeness	ProductionVolume	2.7 Mt in Europe in 2000
Representativeness	SamplingProcedure	literature values based on company survey
Representativeness	Extrapolations	no extrapolation
Representativeness	UncertaintyAdjustments	none

87 Trimethylamine

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 (Additions: Christian Capello, ETHZ)
 Review: Roland Hischier, EMPA St. Gallen

87.1 Introduction

Trimethylamine ($(\text{CH}_3)_3\text{N}$, CAS-No. 75-50-3, synonyms: TMA, N,N-dimethylmethamine, N,N-dimethylmethanamine) is at room temperature a colourless, highly flammable gas with an odour of ammonia. For this inventory the functional unit is 1 kg of anhydrous trimethylamine. The most important chemical and physical properties of trimethylamine used in this inventory are given in the following table.

Tab. 87.1 Chemical and physical properties of trimethylamine

Property	Unit	Value	Remarks
Molecular weight	g mol^{-1}	59.11	
Specific gravity	kg m^{-3}	640	at 20 °C
Boiling point	°C	2.9	at normal pressure

87.2 Reserves and resources of material

Commercial production of trimethylamine is based on the catalytic alkylation of anhydrous ammonia with methanol (methyl alcohol). Most production plants produce trimethylamine together with mono-methylamine and di-methylamine. The production of trimethylamine is also possible from formaldehyde instead of methanol (Wells 1991). For this inventory only the production of trimethylamine from methanol was investigated.

87.3 Use of material / product

According to Wells 1991, the main application of trimethylamine is the production of chlorine chloride. Another application of trimethylamine is in the production of strong base anion exchange resins (activation step). There was no information available on the amount of production and use within Europe.

87.4 Systems characterization

In the production process for trimethylamine, the main raw materials, an approximation of the production energy and estimations for the emissions to water and air were considered. This module represents only a rough estimation of the process requirements and should be used only for processes where the impact of trimethylamine is not considered to be high.

For this inventory the functional unit is 1 kg trimethylamine (anhydrous). As process location, Europe (RER) was used. The process chain was assessed as shown in the following figure.

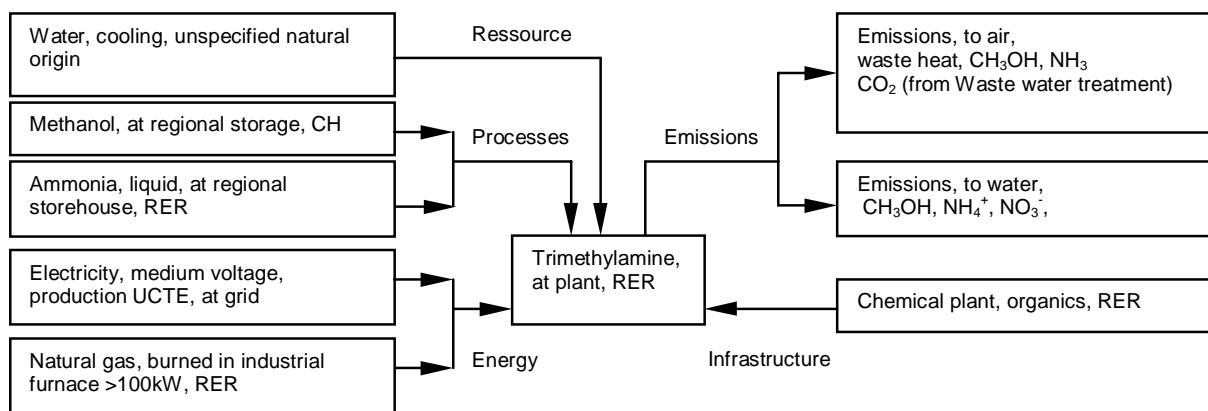


Fig. 87.1 Process chain for the production of trimethylamine

87.5 Trimethylamine, at plant (location: RER)

87.5.1 Process

Due to missing production data, this inventory about the production process for trimethylamine bases on stoichiometric calculations. In the calculations, a process yield of 95% for the used chemicals was assumed (Wells 1991). The emissions to air and water were estimated using mass balances. It was assumed that the wastewater is treated in an internal wastewater treatment plant. To estimate the process energy demand, these values were approximated with data from a large chemical plant site (Gendorf 2000). Due to these approximations the uncertainty within the results of this inventory is large.

According to Wells 1991, the production of methylamine is carried out with vaporised methanol and ammonia in a mol ratio of 1:2. The raw material stream is mixed with the recycled amine and ammonia feed pre-heated to 350 °C and reacted at a pressure of 14 bar and about 450 °C. As catalysts for the reaction, aluminium silicate or phosphate are used. Trimethylamine is recovered overhead of the distilling column. In this process, trimethylamine is produced together with di-methylamine and mono-methylamine, which are recovered by further distillation of the methylamine mixture recovered from the bottom of the distilling column. Depending on the desired product, the methanol-ammonia ratio may be adjusted in the production (1:1.5 for trimethylamine to 1: 4 for mono-methylamine).

For this inventory the production of di-methylamine and mono-methylamine were not considered because there were no process specific data available and the inventory data is based on stoichiometry. Also the catalysts used for the reaction were omitted due to missing data on the amounts used. It was assumed that they do not have an important contribution on the final result of the inventory.

A simplified process scheme of trimethylamine production from methanol and ammonia is shown in Fig. 87.2. The overall reaction for the production of trimethylamine can be formulated as follows:



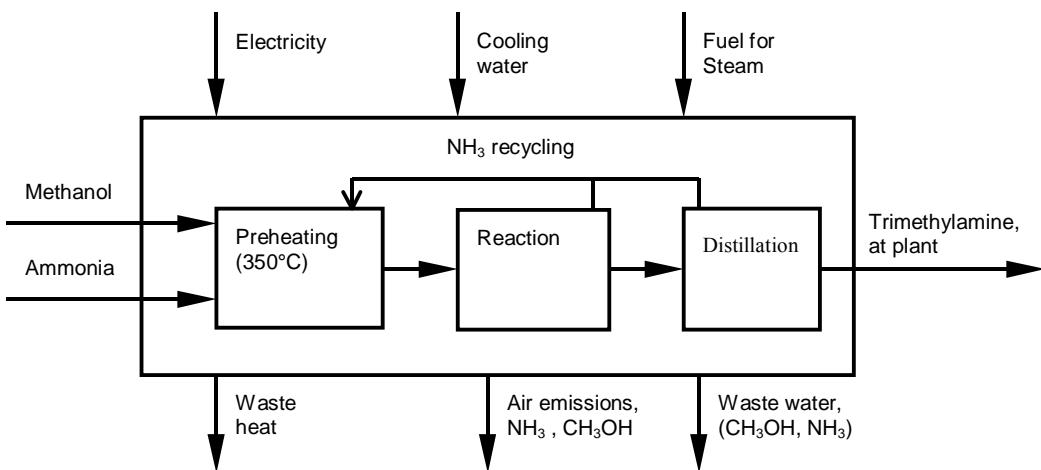


Fig. 87.2 Simplified process for the production of trimethylamine

87.5.2 Resources

Energy

Electricity is needed to run the process auxiliaries and the wastewater treatment. Fossil fuel is needed to generate the desired heat for the preheating and the distillation of the product. There was no information available on the amount of energy used for the production process. These values were estimated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf 2000). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for the energy consumption of the trimethylamine production. This total energy demand was covered with natural gas (50%), electricity (38%), and steam from external energy sources (12%). For this inventory all energy used for heat or steam was assumed to be natural gas. An amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was assumed. A summary of the values used is given in Tab. 87.2.

Raw materials and chemicals

For the production of 1 kg trimethylamine the following stoichiometric inputs are needed (yield 100%):

- Methanol, CH_3OH : 1.626 kg (50.8 mol)
- Ammonia, NH_3 : 0.288 kg (17.0 mol)

A yield of 95% was used, as reported in Wells 1991. To produce 1 kg trimethylamine, 1.71 kg methanol and 0.303 kg ammonia were therefore considered as raw materials in this inventory. The stoichiometric output of water (0.914 kg per kg product) from the process was not considered as co-product. This water was assumed to be disposed with the other wastewater of the process. A summary of the values used is given in Tab. 87.2.

Water use

There was no information available on the amount of cooling water used within the plant. The process cooling water demand was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf 2000). In this plant an average of 24 kg water per kg of product were used for. This value was used in this inventory as approximation for the cooling water consumption of the trimethylamine production. According to IPPC 2000, the cooling water demand may reach 86 kg kWh^{-1} for an once through cooling system, which would lead to a cooling water demand of 48 kg per kg product for the assumed process heat demand of 2 MJ. For other cooling systems (closed circuit) the cooling water demand would be much smaller. For this inventory a value of 0.024 m^3 cooling water per kg product was used.

Transport

Because the processes for the raw materials already include transport to a regional storage, no further transport requirements were considered.

87.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed or 1.2 MJ per kg trimethylamine is converted to waste heat that is released to the air.

Emissions to air

There was no data available on process emissions to air for the production of trimethylamine. Direct emissions of trimethylamine to air were neglected. As approximation, the air emissions occurring from the purge vent, the distillation vent and fugitive emission sources were estimated to 0.2% of the raw material input. This assumption leads to air emissions of 3.42 g methanol and 0.61 g ammonia per kg product.

Emissions to water

The remaining amount of unreacted raw materials was assumed to leave the production process with the wastewater. This assumption leads to a pollution of the wastewater with 82.2 g methanol and 14.6 g ammonia per kg product. Further it was assumed that this wastewater is treated in an internal wastewater plant. The removal efficiency of the wastewater treatment plant was estimated with data from different effluent treatment plants operated within the chemical sector in the EU (IPPC 2002). The removal efficiency for methanol was assumed to be 90% leading to emissions of 8.22 g methanol per kg product in the treated water. The carbon contained in the removed methanol was accounted as CO₂ emissions to air (0.102 kg CO₂ per kg product). For the ammonia within the wastewater a removal efficiency for NH₄-N of 70% and for total N of 50% was assumed. The remaining emissions to water were considered as ammonium (NH₄) and nitrate (NO₃). The nitrogen emitted to air (N₂) or remaining in the sewage sludge was neglected. This assumptions leads to emissions of 4.63 g NH₄ and 106 g NO₃ per kg product in the treated water. The values for COD, BOD, TOC and DOC used in this inventory were calculated from the amounts of methanol, ammonium and nitrate in the treated waste water assuming a carbon conversion of 96% for COD. For the calculation of the values for BOD and DOC the worst-case scenario BOD = COD and TOC = DOC was used. A summary of the values used in this inventory is given in Tab. 87.2.

Solid wastes

Solid wastes generated during the production of trimethylamine, such as spent catalysts, were neglected in this inventory.

Tab. 87.2 Energy demand, resource demand and emissions for the production of trimethylamine.

Resources, emissions	Unit	Value per kg trimethylamine	Remarks
Methanol, at regional storage; ¹	kg	1.71	Stoechiometric calc., 95% yield
Ammonia, at regional storage; ¹	kg	0.303	Stoechiometric calc., 95% yield
Electricity, medium voltage, at grid; ²	kWh	0.333	Estimation
Natural gas, burned in industrial furnace >100kW; ²	MJ	2	Estimation
Water, cooling, unspecified; ²	m ³	$24 * 10^{-3}$	Estimation
Waste heat, to air	MJ	1.2	Calculated from electricity demand
Ammonia (NH ₃), to air	kg	$0.607 * 10^{-3}$	Estimated as 0.2% of the input
Methanol (CH ₃ OH), to air	kg	$3.42 * 10^{-3}$	Estimated as 0.2% of the input
CO ₂ , to air; ³	kg	0.102	From waste water treatment
Ammonia (NH ₄ ⁺), to water; ³	kg	$4.63 * 10^{-3}$	Calculated from mass balance
Nitrate (NO ₃ ⁻), to water; ³	kg	$10.6 * 10^{-3}$	Calculated from mass balance
Methanol (CH ₃ OH), to water; ³	kg	$8.22 * 10^{-3}$	Calculated from mass balance
COD, BOD; ⁴	kg	$9.73 * 10^{-3}$	Calculated from water emissions
DOC, TOC; ⁴	kg	$3.08 * 10^{-3}$	Calculated from water emissions
Chemical plant, organics	Unit	$4 * 10^{-10}$	Approximation for infrastructure

¹ Value for yield from Wells 1991² Approximated with data from a large chemical plant site in Germany (Gendorf 2000).³ 4.8% of input was assumed to be emitted to a waste water treatment plant with an efficiency of 90% for C, 70% for NH₄-N and 50% for N-tot. N is emitted to surface water as NH₄ and NO₃. Eliminated C is emitted as CO₂ to air.⁴ Calculated from methanol and N- emissions using worst case scenario COD = BOD, DOC = TOC

87.5.4 Infrastructure

No information was available about the infrastructure of the production plant. It was assumed that the importance of infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant lifetime of 50 years, an amount of $4 * 10^{-10}$ units per kg trimethylamine was included.

87.6 Data quality considerations

The following table shows the data quality indicators for the inventory of trimethylamine production (location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation, and sample size.

The data in the inventory of the trimethylamine production is highly uncertain, because only few data of the production processes were available. Therefore, the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. The highest uncertainties exist for the process energy demand and the emissions. Due to missing data, these values are based mainly on assumptions and approximations. Especially the uncertainty in the emission data is of importance for the quality of the dataset. Further uncertainty arises from possibly missing auxiliary materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it depends only on the yield-factor used for the stoichiometric calculations. Concerning infrastructure, also an approximation was used because of missing data.

Tab. 87.3 In- / outputs for the module “trimethylamine, at plant”, location GLO

Process output: 1 kg, trimethylamine, at plant, RER						
	Name, Location	Value	Unit	Uncertainty		Comment
				Type	Score	
←	methanol, at regional storage, CH	1.71E+0	kg	lognorm	nA,nA,nA,nA,nA,nA	1.05 Uncert. calculated for process yield 90-99.8%
	ammonia, liquid, at regional storehouse, RER	3.03E-1	kg	lognorm	nA,nA,nA,nA,nA,nA	1.05 Uncert. calculated for process yield 90-99.8%
	electricity, medium voltage, production UCTE, at grid, UCTE	3.33E-1	kW·h	lognorm	5.5,1,1,4,5	1.88 Approximation with data of a large chem. plant
	natural gas, burned in industrial furnace >100kW, RER	2.00E+0	MJ	lognorm	5.5,1,1,4,5	1.88 Approximation with data of a large chem. plant
	chemical plant, organics, RER	4.00E-10	unit	lognorm	5.5,1,1,4,5	3.55 Approximation with average chem. plant
Emissions	Water, cooling, unspecified natural origin	2.40E-2	m³	lognorm	5.5,1,1,4,5	1.88 Approximation with data of a large chem. Plant
	Heat, waste, to air, high population density	1.20E+0	MJ	lognorm	5.5,1,1,4,5	1.88 Calculated from electricity demand
	Methanol, to air, high population density	3.42E-3	kg	lognorm	5.5,nA,nA,nA,5	2.32 Estimated
	Ammonia, to air, high population density	6.07E-4	kg	lognorm	5.5,nA,nA,nA,5	2.32 Estimated
	Carbon dioxide, fossil, to air, high population density	1.02E-1	kg	lognorm	5.5,nA,nA,4,5	1.88 Estimated from mass balance and WWTP effic.
	BOD5, Biological Oxygen Demand, to water, river	9.73E-3	kg	lognorm	5.5,nA,nA,4,5	2.11 Estimated from mass balance and WWTP effic.
	COD, Chemical Oxygen Demand, to water, river	9.73E-3	kg	lognorm	5.5,nA,nA,4,5	2.11 Estimated from mass balance and WWTP effic.
	DOC, Dissolved Organic Carbon, to water, river	3.08E-3	kg	lognorm	5.5,nA,nA,4,5	2.11 Estimated from mass balance and WWTP effic.
	TOC, Total Organic Carbon, to water, river	3.08E-3	kg	lognorm	5.5,nA,nA,4,5	2.11 Estimated from mass balance and WWTP effic.
	Methanol, to water, river	8.22E-3	kg	lognorm	5.5,nA,nA,4,5	3.55 Estimated from mass balance and WWTP effic.
(1) From technosphere, 2) Ressources	Ammonium, ion, to water, river	4.63E-3	kg	lognorm	5.5,nA,nA,4,5	2.11 Estimated from mass balance and WWTP effic.
	Nitrate, to water, river	1.06E-2	kg	lognorm	5.5,nA,nA,4,5	2.11 Estimated from mass balance and WWTP effic.

87.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

87.8 Conclusions

The quality of the inventory for trimethylamine production depends strongly on the data used for the emissions and the yield. For further work on this inventory these data should be improved by using data from specific plants within Europe. This would also improve the data used for energy consumption and infrastructure.

87.9 References

- | | |
|--------------|---|
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88 Unspecified chemicals

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 Review: Heiko Kunst, TU Berlin

88.1 Introduction

For all cases, where there is no information about the specific chemical substance but an indication of the amount of chemicals used, unspecified chemical modules - one for organic substances and another one for anorganic substances - are established within this study. The following paragraph describes how these modules are established.

88.2 Production of Chemicals

In 2001 the worldwide production of chemicals was in the order of 1.632 billion Euros, with Europe accounting for about 32% of it (CEFIC (2002)). Within this, the European production covers a wide range of different chemical products, as shown in Fig. 88.1.

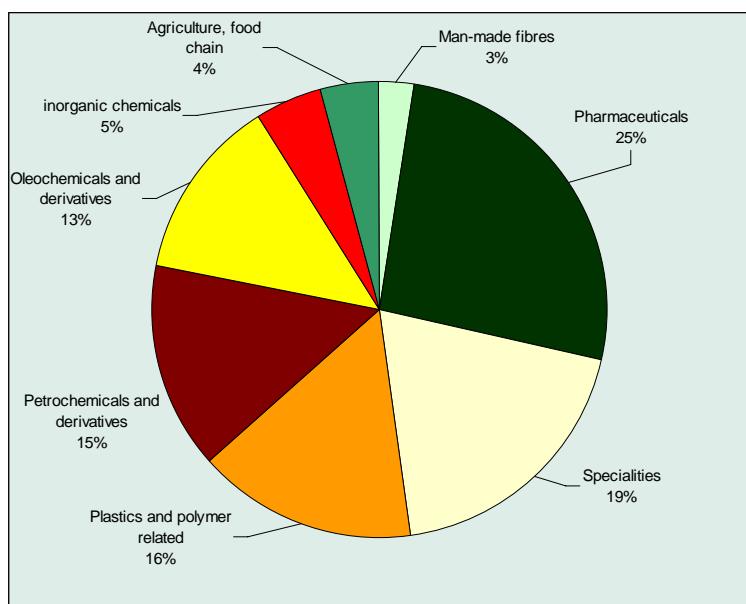


Fig. 88.1 Percentages of European chemical output in 2001 (from CEFIC (2002))

According to Chenier (1992), sulfuric acid is the most produced chemical worldwide. In 2001, Germany, France, UK and Italy produced around 17'986 million pounds of this substance (C & EN (2002): 78). In organic chemistry, some 70'000 different substances are produced worldwide - with ethylene on the top of the list. Total European production in 2001 was around 43.4 billion pounds (C & EN (2002): 78). It is the leader of the basic seven organics (ethylene, propylene, butadiene, benzene, toluene, xylene and methane). According to Chenier (1992), the top 50 chemicals consist of 21 inorganic and 29 organic substances with a total volume of about 630 billion pounds. Thereof, 65% are inorganics and only 35% are organics. As no newer information is available, this ranking is used within this study. Tab. 88.1 shows an overview of the top organic and inorganic chemicals by weight, based on informations from Chenier (1992).

Tab. 88.1 The top organic and inorganic chemicals by weight (from Chenier (1992))

	Organic chemicals	Inorganic chemicals
1	Ethylene	Sulphuric Acid
2	Propylene	Nitrogen
3	Urea	Oxygen
4	Ethylene dichloride	Lime
5	Benzene	Ammonia
6	Vinyl chloride	Phosphoric acid
7	Ethlybenzene	Sodium hydroxide
8	Styrene	Chlorine
9	Methanol	Nitric acid
10	Terephthalic acid	Sodium carbonate
11	Formaldehyde	Ammonium nitrate
12	MTBE	Carbon dioxide
13	Toluene	Ammonium sulphate
14	Xylene	Hydrochloric acid
15	Ethlyene oxide	Potash
16	p-Xylene	Carbon black
17	Ethylene glycol	Aluminium sulphate
18	Cumene	Titanium dioxide
19	Acetic acid	Sodium silicate
20	Phenol	Sodium sulphate
21	Propylene oxide	Calcium chloride
22	Butadiene	Chlorofluorocarbons
23	Acrylonitrile	Lignosulphonic acid salt
24	Vinyl acetate	Phosphorus
25	Cyclohexane	Sodium bicarbonate
26	Acetone	Hydrofluoric acid
27	Adipic acid	Potassium hydroxide
28	Isopropanol	Sodium chlorate
29	Caprolactam	Sulphur dioxide
30	Phosgène	Hydrogen peroxide

88.3 Systems characterization

In this study, the first 20 substances from Tab. 88.1 that are included into the ecoinvent database are taken for establishing the two unspecific chemical datasets. As there are only the production volumes for a small part of the substances mentioned in Tab. 88.1 available from literature sources, an unweighted average of the included chemical substances was used within this study. Fig. 88.2 shows the examined systems.

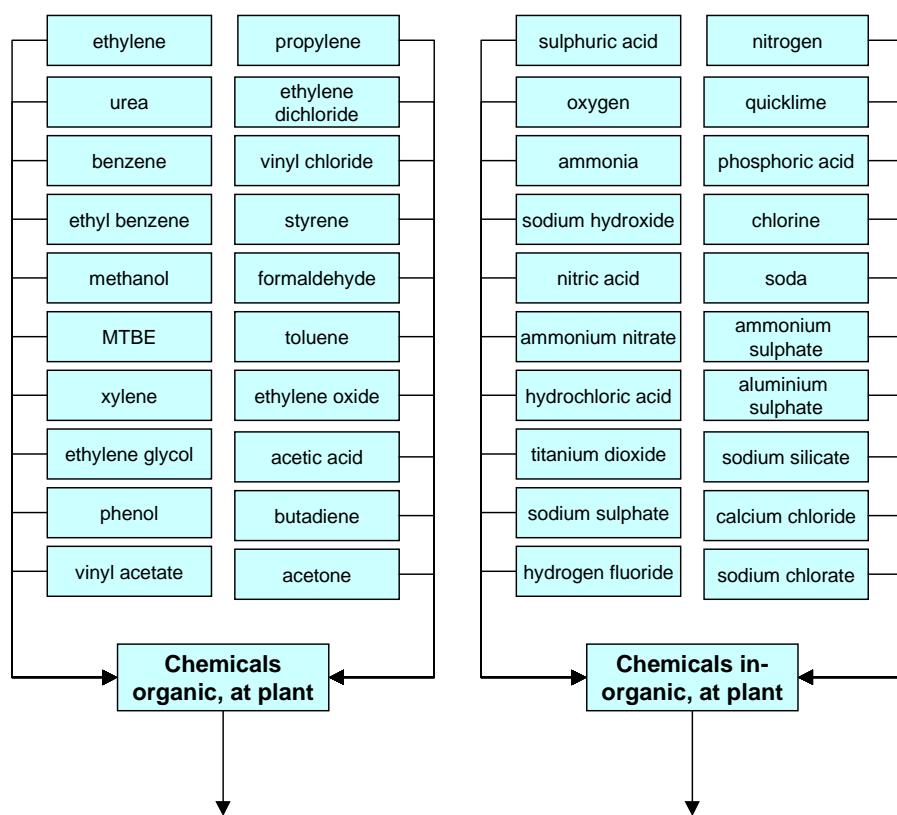


Fig. 88.2 System boundaries of the two unspecific chemicals modules

88.4 Process data

Data source for all chemicals used according to Fig. 88.2 is the respective dataset established within this project. They are described in details in the different reports of this study (Althaus et al. (2003); Hischier (2003); Kellenberger et al. (2003); Nemecek et al. (2003)).

88.5 Data quality considerations

Both established datasets represent not more than a first estimation. As this dataset is used in cases where the exact composition of a substance is not known, it is not possible to make general remarks about how good this dataset fits in these different cases. Therefore the fact to establish an unweighted average dataset on the basis of the most produced substances is not better or worse than a weighted average, with the weighting based on the present production volumes of the different chemicals.

The resulting data together with their respective uncertainty values for the two datasets „chemicals organic, at plant“ and „chemicals inorganic, at plant“ are shown in Tab. 88.2 and Tab. 88.3. Additionally, the most important fields of the ecoinvent meta information from these datasets are listed in chapter 88.8.

Tab. 88.2 In-/Outputs an uncertainty informations for the dataset „chemicals organic, at plant“

Explanation	Name	Location	Unit	chemicals organic, at plant		GeneralComment	
				GLO	UncertaintyType		
					kg		
Input from Technosphere	ethylene, average, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	propylene, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	urea, as N, at regional storehouse	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	ethylene dichloride, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	benzene, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	vinyl chloride, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	ethyl benzene, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	styrene, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	methanol, at plant	GLO	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	formaldehyde, production mix, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	methyl tert-butyl ether, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	toluene, liquid, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	xylene, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	ethylene oxide, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	ethylene glycol, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	acetic acid, 98% in H ₂ O, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	phenol, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	butadiene, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	vinyl acetate, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	acetone, liquid, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
Output	chemicals organic, at plant	GLO	kg	1			

Tab. 88.3 In-/Outputs an uncertainty informations for the dataset „chemicals inorganic, at plant“

Explanation	Name	Location	Unit	chemicals inorganic, at plant		GeneralComment	
				GLO	UncertaintyType		
					kg		
Input from Technosphere	sulphuric acid, liquid, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	nitrogen, liquid, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	oxygen, liquid, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	quicklime, milled, loose, at plant	CH	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	ammonia, liquid, at regional storehouse	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	phosphoric acid, industrial grade, 85% in H ₂ O, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	chlorine, liquid, production mix, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	nitric acid, 50% in H ₂ O, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	soda, powder, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	ammonium nitrate, as N, at regional storehouse	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	ammonium sulphate, as N, at regional storehouse	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	hydrochloric acid, 30% in H ₂ O, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	aluminium sulphate, powder, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	titanium dioxide, production mix, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	sodium silicate, spray powder 80%, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	sodium sulphate, powder, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	calcium chloride, CaCl ₂ , at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	hydrogen fluoride, at plant	GLO	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
	sodium chlorate, powder, at plant	RER	kg	5.00E-02	1	1.69 (5,5,3,3,3,5); estimated, based on most produced chemicals	
Output	chemicals inorganic, at plant	GLO	kg	1			

88.6 Cumulative results and interpretation

Results of the cumulative inventory from both datasets can be downloaded from the database.

88.7 Conclusions

The inventories for both unspecific chemical datasets are based on literature and represent a rough estimation. These dataset should be used only when no information about the actual chemical substance are known.

88.8 EcoSpold Meta Information

ReferenceFunction	Name	chemicals organic, at plant	chemicals inorganic, at plant
Geography	Location	GLO	GLO
ReferenceFunction	InfrastructureProcess	0	0
ReferenceFunction	Unit	kg	kg
ReferenceFunction	IncludedProcesses	A general module for organic chemicals is established, based on the modules of several organic substances from the ecoinvent database	A general module for inorganic chemicals is established, based on the modules of several inorganic substances from the ecoinvent database
ReferenceFunction	Amount	1	1
ReferenceFunction	LocalName	Chemikalien organisch, ab Werk	Chemikalien anorganisch, ab Werk
ReferenceFunction	Synonyms		
ReferenceFunction	GeneralComment	An unweighted average of the first 20 organic substances, being part of the top100 chemicals and included into this database, is established.	An unweighted average of the first 20 inorganic substances, being part of the top100 chemicals and included into this database, is established.
ReferenceFunction	InfrastructureIncluded		
ReferenceFunction	Category	chemicals	chemicals
ReferenceFunction	SubCategory	organics	inorganics
ReferenceFunction	LocalCategory	Chemikalien	Chemikalien
ReferenceFunction	LocalSubCategory	Organisch	Anorganika
ReferenceFunction	Formula		
ReferenceFunction	StatisticalClassification		
ReferenceFunction	CASNumber		
TimePeriod	StartDate	2000-01	2000-01
TimePeriod	EndDate	2000-12	2000-12
TimePeriod	DataValidForEntirePeriod	1	1
TimePeriod	OtherPeriodText		
Geography	Text	General module, based on chemicals from Europe, Switzerland and Global level, used as a global average.	General module, based on chemicals from Europe, Switzerland and Global level, used as a global average.
Technology	Text	Present technology for the production of the different included chemicals (for details, see datasets of the respective chemical substance)	Present technology for the production of the different included chemicals (for details, see datasets of the respective chemical substance)
Representativeness	Percent		
Representativeness	ProductionVolume	unknown	unknown
Representativeness	SamplingProcedure		
Representativeness	Extrapolations	see GeneralComment	see GeneralComment
Representativeness	UncertaintyAdjustments		

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89 Urea-formaldehyde resin and melamine-formaldehyde resin

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89.1 Introduction

Amino resins are thermosetting polymers made by combining an aldehyde with a compound containing an amino (-NH₂) group. Urea-formaldehyde accounts for over 80% of amino resins; melamine-formaldehyde accounts for most of the rest. (Other aldehydes and other amino compounds are used to a very minor extent.)

The principal attractions of amino resins and plastics are:

- water solubility before curing, which allows easy application to and with many other materials,
- colourlessness, which allows unlimited colorability with dyes and pigments,
- excellent solvent resistance in the cured state,
- outstanding hardness and abrasion resistance, and
- good heat resistance.

Limitations of these materials include release of formaldehyde during cure and, in some cases, such as in foamed insulation, after cure, and poor outdoor weatherability for urea mouldings, to mention the most important.

The term *amino resin* is usually applied to the broad class of materials regardless of application, whereas the term *aminoplast* or sometimes *amino plastic* is more commonly applied to thermosetting moulding compounds based on amino resins. The following description of resources, physical and chemical properties, production technology and use of amino resins are summarised from Diem (2000) and Williams (2002).

89.2 Reserves and Resources

Urea resins are produced basically from urea, melamine and formaldehyde. Therefore, the resources available as well as the reserves are the same as for the production of these substances, described in the corresponding chapter. Since only approximately 10% of the total urea production is used for amino resins, they appear to have a secure source of low cost raw material. Additionally, the future for amino resins seems secure because they can provide qualities that are not easily obtained in other ways.

The production of amino resins in the OECD countries was 1983 2.7 Mio Tons. From these, 1.4 Mio Tons corresponds to Europe.

The technology is highly developed, so that there are little improvements expected in the manufacturing process. New developments will probably be in the areas of more highly specialised materials for treating textiles, paper, etc, and for use with other resins in the formulation of surface coatings, where a small amount of an amino resin can significantly increase the value of a more basic material. Additionally, since amino resins contain a large proportion of nitrogen, a widely abundant element, they may be in a better position to compete with other plastics as raw materials based on carbon compounds become more costly.

89.3 Physical and chemical properties of amino resins

89.3.1 Physical Properties

Amino resins are available commercially as concentrated solutions or solids, e.g. powders. The solutions generally contain water as a solvent, but in the surface-coating resins the solvents are alcohols. The solutions range from colourless and clear to milky and cloudy and are tacky to the touch. Their viscosities are substantially higher than that of water, in general from 200 to 2000 mPa·s –measured at 20 °C. The amino resins can be odourless or, depending on the content of free formaldehyde, have a more or less sharp odour. The densities of the solutions at the commercially available concentrations of 55 – 80 % solids are from 1.23 to 1.31 g/cm³. An important property of the resins is the amount of water that can be added without precipitating solids. At relatively low temperatures, i.e., below about 20 °C, pronounced cloudiness and an unusually large increase in viscosity are observed in many cases.

Some resin solutions exhibit the phenomenon of pseudoplasticity (thixotropy), which may or may not be desirable. Thixotropy means that the viscosity decreases as the shearing force increases. In powder form amino resins are white. In the spray-dried, commercially available form they have a particle size generally of 15 – 70 µm, but always < 200 µm. This particle size is a result of the spray-drying process.

The bulk density of the commercially available products is 0.5 – 0.8 kg/L. The powder resins dissolve in water to give milky liquids. Flourlike additives can be mixed with some resins, which then assume the colour of the additive to a greater or lesser extent.

89.3.2 Chemical Properties

Even when they are prepared from only two components, the amino resins are mixtures of various substances. For example, in the case of urea–formaldehyde resins the major components of the mixture are various hydroxymethyl compounds and oligomers composed of different combinations of basic units and substituted basic units. Hence, it is not possible to attribute specific chemical properties to these substances, as in the case of a pure compound.

89.4 Production technologies for urea resins

Fig. 89.1 shows the manufacturing processes from urea-formaldehyde and melamine-formaldehyde resins.

89.4.1 Raw Materials

Many large chemical companies produce amino resins and the raw materials needed, i.e., formaldehyde, urea, and melamine.

In the production of amino resins, **formaldehyde** is used either in the form of solid paraformaldehyde, in aqueous solution, or as a urea–formaldehyde precondensate containing from 4 to 5 mol of formaldehyde per mol of urea. Paraformaldehyde is a mixture of hydrated polyoxymethylene molecules, with a degree of polymerisation of 6 – 100 units. The most frequently used commercial form is a 30 – 55% aqueous solution of formaldehyde. Finally, aqueous solutions of urea–formaldehyde precondensates also are employed. Commercially available solutions contain from 70 to 80 % of the active ingredients, calculated as urea and formaldehyde.

Urea is available commercially as a white crystalline product or as prills. For amino resin production, a technical-grade product is usually adequate. In the production of amino resins, urea is employed in solid form, in solution, or as a urea–formaldehyde precondensate. Urea is soluble in water, and the crystalline solid is somewhat hygroscopic, tending to cake when exposed to a humid atmosphere. For this reason, urea is frequently palletised or prilled (formed into little beads) to avoid caking and making it easy to handle.

Melamine is a white powder that sublimes on heating. The particle diameter depends on the production process and varies from 5 to 300 µm. The rate of solubility in formaldehyde solutions depends on the particle size and is an important parameter given by the producers. The colour number of a 50 % melamine – formal-

dehydye solution may not exceed 20 (APHA). This is important with respect to raw materials for surface coatings and to impregnating resins.

89.4.2 Principle aspects of the production of amino resins

Amino resin production consists of two stages: *hydroxymethylation* and *condensation*. Depending on the reaction conditions, hydroxymethylation is accompanied to a greater or lesser extent by condensation. The following equations illustrate the process for formaldehyde plus urea:

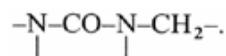
- Hydroxymethylation:



- Condensation:



- Further condensation leads to longer chains of the basic unit



The process for the production of the resin is continued until the resulting product is an oligomeric mixture that is still soluble or fusible. It is protected against further condensation by rendering the medium alkaline.

Hydroxymethylation

Hydroxymethylation can be carried out using either alkaline or acid catalysis, but the former is faster. The hydroxymethylation of urea is slightly exothermic. Industrial processes produce variable mixtures of oligomers with mixed repeat units, so the overall reaction rate is also variable and cannot be defined. Moreover, the important resin properties have not been correlated with the individual reaction rates. In general, the hydroxymethylation rate increases with increased concentration, temperature, and pH. Substituents also have an effect; adjacent electron-withdrawing groups reduce the reaction rate, as do bulky substituents.

Condensation

The condensation is catalysed by acids since the methylene bonds between two urea molecules are very stable and can be hydrolysed only by strong acids at elevated temperatures. The condensation reaction is slightly exothermic. It is impossible to give a single reaction rate for the condensation process because there are many different starting materials (hydroxymethyl compounds) and many end products (methylene compounds). The type of solvent also has an effect on the condensation rate.

Condensation of the resin by means of acid catalysis, i.e., cross-linking to give a substantially infusible product, is not carried out until the resin is put to use. This process is called *curing*. However, free hydroxymethyl groups are present even in this state. Condensations carried out in an excess of an alcohol, with the addition of acid and removal of water as necessary, produce curable etherified amino resins. These are soluble in nonaqueous solvents and can be mixed with alkyd resins, epoxy resins, etc. They are used as starting materials in the production of surface coatings. Resin glues based on urea have been subjected to partial ethoxylation to stabilise them against further condensation.

89.4.3 Production processes of amino resins

Amino resins usually are prepared in 5 – 20 m³ batches. However, continuous processes are employed also, particularly for the production of resin glues. The patent literature describes processes where a particular stage is operated continuously while other stages are operated batchwise. In general, and because the reaction

rate and the composition of the end product are influenced by a large number of parameters, the reaction must be controlled carefully. Only the most important processes are described here since there is a large number of reaction parameters and resultant adaptations of the process.

Batchwise Production

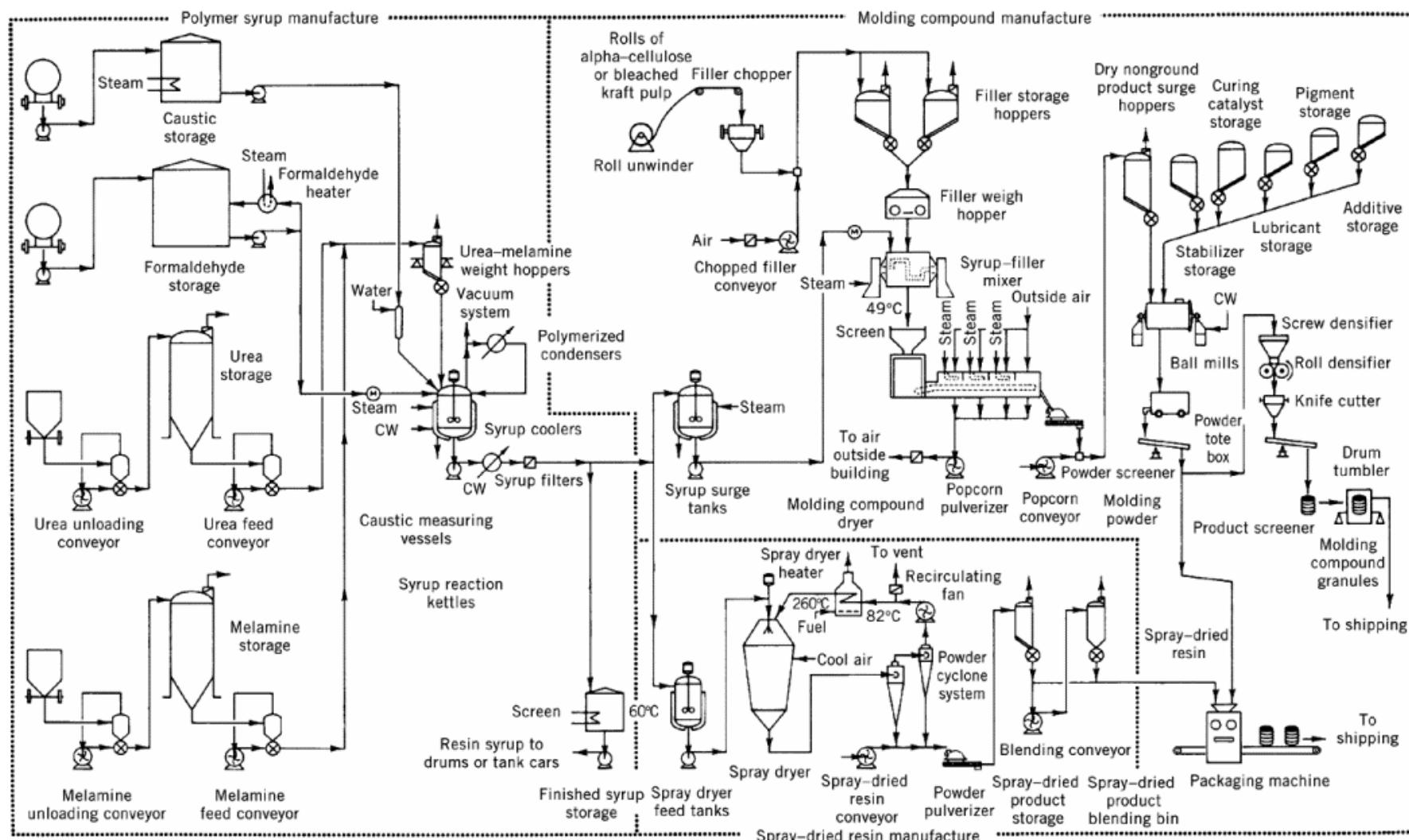
The batchwise procedure is the most widely used method for the industrial production of amino resins. Its disadvantage is its relatively small production capacity but on the other hand, this process permits an extensive variety of products and frequent changes of product.

The reactions are carried out in stirred kettles, in two or more stages, at 70 – 100 °C. In the first stage, which is carried out in a slightly acidic to alkaline solution, the principal reaction is hydroxymethylation. In subsequent stages, the condensation is carried out, water is split off, and higher molecular weight products of increasing viscosity are obtained. When the condensation is complete, the product is evaporated in the stirred kettle, or more economically in a tubular vaporiser, with the pressure reduced to protect the resin. The quality of the resin is then compared to its specifications and it is discharged into a storage container.

Continuous Production

The disadvantages of continuous production are that the amount produced per unit time in a particular plant can vary only within relatively narrow limits because prolonged residence under otherwise constant conditions increases the proportion of molecules with high degrees of condensation. Changing product is not simple either. Thus, the continuous production process is employed where the variety of products is restricted to a relatively narrow range. On the other hand, continuous procedures give a very uniform product quality. There are a large number of continuous processes that differ only in process technology for the product flow. In general, the differences include variations in the temperature, pH, concentration, or modifiers. In a typical example, urea and formaldehyde are combined and the solution pumped through a multistage unit. The product is then concentrated in a continuous evaporator to about 60–65% solids

Fig. 89.1 Urea-formaldehyde and melamine-formaldehyde resin manufacture. (Taken from Williams (2002): Fig. 2)



CW: cold water

89.5 Use

Amino resins find their major use as adhesives. They are used in the production of plywood, wafer-board, strandboard, and particle board. Other types are employed for the production of laminated beams and parquet flooring, and for furniture assembly. Amino resins are also used to strengthen paper, to produce moulding compounds and the flexible backing of carpets, as leather auxiliaries and soil conditioners, and for protective surface coatings. The largest amount of amino resins is consumed by the woodworking industry.

New uses are being developed constantly and any list is bound to be incomplete. The importance of many uses, e.g., flameproofing agents, has declined greatly. Some applications, e.g., casting resins, have proved unsatisfactory in practice, whereas others are only at the development stage and their industrial suitability cannot yet be assessed. Tab. 89.1 summarises the principal uses for amino resins.

Tab. 89.1 Uses for amino resins (Taken from Diem 2002. Table 6)

Application	Resin and use
Binders for glass fibre webs	Reinforcing glass fibres in webs by means of urea resins
Foams	Soil conditioning, covering landfills, heat insulation, lining tunnels in mines.
Foundry sand binders	Binders for sand-casting in the foundry industry; casting moulds and cores; modification with furfuryl alcohol
Concrete liquefiers and auxiliaries for building materials	Sulphite-modified melamine resins
Flame-proofing agents	Flameproofing wood by means of amino resins containing phosphorus, boron, bromine, etc.
Ion-exchange resins	Melamine-formaldehyde condensates modified with amines Used for recovering silver from photographic effluents
Coatings for abrasive papers	Urea – formaldehyde – furfuryl alcohol condensates for imparting water-resistance
Wood preservatives	Melamine – formaldehyde condensates impart good ageing resistance; no shrinkage; no seasoning cracks
Microcapsules	Urea – formaldehyde resins
Firelighters	Emulsion of urea – formaldehyde resin with a liquid fuel and hardeners is processed to give small mouldings. Lighting oil-fired furnaces, charcoal grills, etc.
Sewage flocculants	Urea – formaldehyde resins cause flocculation

89.6 System characterisation

This report corresponds to the modules in the ecoinvent database: **Production of 1 kg urea-formaldehyde resin, at plant, in Europe**, and **Production of 1 kg melamine-formaldehyde resin, at plant, in Europe**.

According to Williams 2002, the typical plant considered for this study is the plant as shown in Fig. 89.1. **All data are referred to 1 kg resin 100%.**

The system includes the process with the consumption of raw materials, energy, infrastructure and land use, as well as the generation of emissions to air and water. It also includes transportation of the raw materials. Due to the lack of data, no values for auxiliaries or solid wastes can be presented and therefore, transportation and consumption of auxiliaries as well as generation and transportation of wastes are not included. It does not include transportation of the final product resin. There are no by-products generated in the production process.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage is also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

89.7 Urea-formaldehyde and melamine-formaldehyde resin production process

89.7.1 Data source

With exception of values for the main raw materials, no data is available in literature for inputs and outputs of the production process of both formaldehyde resins analysed in this study. Therefore, data for the manufacturing of alkyd resin is used as a rough approximation. These data are taken from von Däniiken *et al.* (1995), a study from the Swiss Agency for the Environment, Forests and Landscape (BUWAL). The module used is “alkydharz, mittelölig 60% in Lackbenzin/Xilol 3:1” and bases on confidential data from a European manufacturing company. Unfortunately, there is no further information about this company or the way the data have been acquired and thus, it is difficult to assess the representativeness of these data.

89.7.2 Raw materials and auxiliaries

Amino resins are very variable in their composition. Not only the ratio formaldehyde to urea or to melamine can be very variable according the intended use, but also also the degree of condensation performed and the amount of additives used vary.

In regard to urea-formaldehyde resins, Diem (2000) presents numbers for a typical single resin for particle board production, manufactured according batch production. Basing on the numbers given in this source, it is calculated that for the production of 1 kg 100% resin, 0.49 kg formaldehyde and 0.59 kg urea are needed. (The envolved process has consequently, an efficiency of 93%). These numbers can be compared with the theoretical values obtained from the formula in Section 1.4.2 describing the hydroxymethylation step. In this formula, it can be seen that 1 mol urea and two mol formaldehyde are needed in the formation of the corresponding resin monomer. For this study, it is assumed that of 1 mol final product (100% resin) = 1 mol resin monomer. This means neglecting not only the condensation step but also the addition of additives and auxiliaries, as well as the fact that the final product consists of mixed polymers and fundamentally, that these values refere only to batch production. The resulting values (0.5 kg urea and 0.5 kg formaldehyde) are not very far from the mentioned in Diem 2000. Nevertheless, for this study, the values from the mentioned source are preferred.

Diem (2000) presents numbers also for a typical melamine-formaldehyde resin for the impregnation of paper webs used in producing decorative laminates. Basing on these numbers (also for batch production) and assuming the same process efficiency as mentioned in this source for the manufacturing of u-f resin (93%), for 1 kg 100 % resin, 0.31 kg formaldehyde and 0.77 kg melamine are required. Mombächer (1988) indicates a consumption of 2 to 3 mol formaldehyde and 1 mol melamine for the production of 1 mol melamine-formaldehyde resin. As for urea-formaldehyde above, it is assumed that of 1 mol final product = 1 mol resin monomer. Thus, the following values are obtained for the production of 1 kg melamine-formaldehyde resin: 0.68 kg melamine and 0.32 kg formaldehyde (considering 2.5 mol formaldehyde). For this study, the numbers based on Diem (2000) are taken.

In the sources consulted, there is no information about amount of auxiliaries or water consumed in the manufacturing process.

89.7.3 Energy and transportation

The information regarding consumption of energy for alkyd resin as presented in von Däniken *et al.* (1995), is shown in Tab. 89.2.

Tab. 89.2 Consumption of energy in the production of amino resin (Basing on data for alkyd resin in von Däniken *et al.* 1995)

Input		(kg ⁻¹ 100% amino resin) ¹
electricity	kWh	1.30 E-02
hardcoal	MJ	9.50 E-01
heavy fuel oil	MJ	5.60 E-01
light fuel oil	MJ	1.25 E-01
natural gas	MJ	1.42 E+00

¹: urea-formaldehyde resin or melamine-formaldehyde resin.

In regard to transportation of raw materials, no information about distances is available in the examined data sources. Therefore, for the transportation of raw materials, standard distances as defined in Frischknecht *et al.* (2003) were used: 100 km by lorry 32t and 600 km by train. Tab. 89.3 and Tab. 89.4 summarise the total transport amounts and means for the production of 1 kg of 100% urea-formaldehyde resin and 1 kg of 100% melamine-formaldehyde resin, respectively.

Tab. 89.3 Total transport amounts and means for the production of urea-formaldehyde resin.

(tkm. kg ⁻¹ 100% urea-formaldehyde resin)	lorry	train
raw material	1.08 E-01	6.48 E-01
Auxiliaries	nd	nd
waste to disposal sites	nd	nd
Total transports	1.08 E-01	6.48 E-01

Tab. 89.4 Total transport amounts and means for the production of melamine-formaldehyde resin.

(tkm. kg ⁻¹ 100% melamine-formaldehyde resin)	lorry	train
raw material	1.08 E-01	6.48 E-1
Auxiliaries	nd	nd
waste to disposal sites	nd	nd
Total transports	1.08 E-01	6.48 E-01

nd: no data available

89.7.4 Infrastructure and land use

There is no information available about infrastructure and land-use of amino resins plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. This estimated value is 4.00 E-10 unit. kg⁻¹ resin.

89.7.5 Emissions to air and water

Even if efforts are made to recover and recycle the raw materials, there may be some loss of formaldehyde, or other solvent as tanks and reactors are vented. On the other hand, the amounts of material evolved in curing the resins may be small so that it may be difficult to justify the installation of complex recovery equipment.

According to Diem (2000), the waste gas is treated with water-washing, catalytic combustion, or thermal combustion. von Däniken *et al.* (1995) mention an emission of 1.00 E-03 kg formaldehyde to air per kg resin manufactured, being this a so-called process emission. The emissions due to the consumption of energy are included in the modules concerning use of energy and therefore are not further discussed here.

In regard to wastewaters, Diem (2000) indicates that the condensed vapours or effluents from amino resin production have to undergo biological treatment prior to be released to water. Wastewaters or partially hardened residues inevitably result when machines and containers are cleaned. If the wastewater contains predominantly urea or formaldehyde, it can be reused in the production process. Otherwise, it is eliminated, for example, by incineration. The biologic treatment of industrial effluents from amino resin production is carried out primarily because of the formaldehyde present in them, which is toxic.

In the sources consulted there is no information available on numbers for emissions into air or water arised in the manufacturing process.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. Basing on this assumption the necessary conversion from kWh to MJ is done according to Frischknecht *et al.* (2003). Thus, considering the energy input of 1.30 E-02 kWh. kg⁻¹ resin, the value of waste-heat taken for this study is 4.68 E-02 MJ.kg⁻¹ resin.

89.7.6 Solid wastes

Amino resins can be solidified by hardening them with ammonium chloride or phosphoric acid, or they can be absorbed in sawdust or sand. In this form, they may be deposited in a landfill. Information about amounts of solid wastes generated is not available in the source used.

89.8 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size. Numbers for the consumption of formaldehyde, urea and melamine, are taken from Diem (2000), a high reliable source. Nevertheless, the representativeness of these literature data is difficult to assess for the European scenario. The other values presented in this study are a rough approximation on values corresponding to the manufacture of another type of resin (alkyd resin). Additionally, von Däniken *et al.* (1995) base their numbers for alkyd resins on data provided by a European manufacturing company from which there is no further information. The mentioned factors lead to higher uncertainty scores.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht *et al.* (2003) (transport) resp. the very general module of an organic chemical plant are used.

Tab. 89.5 and Tab. 89.6 summarise the input and output data as well as the uncertainties used for the production of both formaldehyde resins analysed in this study. The values are given for the production of 1 kg of 100% resin. Additionally, the most important fields of the ecoinvent meta information from this dataset are listed in chapter 89.11.

Tab. 89.5 Input- / Output-data for the production of urea formaldehyde resin (expressed per kg 100% resin)

Explanation	Name	Location	Unit	<i>urea formaldehyde resin, with hardener, at plant</i>	<i>RER o kg</i>	UncertaintyType	StandardDeviation95%	GeneralComment	
								Location	InfrastructureProcess
								Unit	
Input from Technosphere	formaldehyde, production mix, at plant	RER	kg	4.90E-1	1	1.32	(3,5,2,2,1,5); data from survey in literature (Diem 2000)		
	urea, as N, at regional storehouse	RER	kg	5.90E-1	1	1.32	(3,5,2,2,1,5); data from survey in literature (Diem 2000)		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.30E-2	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	hard coal, burned in industrial furnace 1-10MW	RER	MJ	9.50E-1	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	5.60E-1	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	heat, light fuel oil, at industrial furnace 1MW	RER	MJ	1.25E-1	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	natural gas, burned in industrial furnace >100kW	RER	MJ	1.42E+0	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	transport, lorry 32t	RER	tkm	1.08E-1	1	2.05	(4,na,na,na,na,na); standard distances		
	transport, freight, rail	RER	tkm	6.48E-1	1	2.05	(4,na,na,na,na,na); standard distances		
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); estimation		
OUTPUTS	urea formaldehyde resin, with hardener, at plant	RER	kg	1.00E+0					
air emission	Heat, waste		MJ	4.68E-2	1	1.42	(3,5,3,3,3,5); calculated from electricity input		
	Formaldehyde		kg	1.00E-3	1	5.19	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		

Tab. 89.6 Input- / Output-data for the production of melamine formaldehyde resin (expressed per kg 100% resin)

Explanation	Name	Location	Unit	<i>melamine formaldehyde resin, at plant</i>	<i>RER o kg</i>	UncertaintyType	StandardDeviation95%	GeneralComment	
								Location	InfrastructureProcess
								Unit	
Input from Technosphere	formaldehyde, production mix, at plant	RER	kg	3.10E-1	1	1.32	(3,5,1,2,1,5); data from survey in literature (Diem 2000)		
	melamine, at plant	RER	kg	7.70E-1	1	1.32	(3,5,1,2,1,5); data from survey in literature (Diem 2000)		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.30E-2	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	hard coal, burned in industrial furnace 1-10MW	RER	MJ	9.50E-1	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	5.60E-1	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	heat, light fuel oil, at industrial furnace 1MW	RER	MJ	1.25E-1	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	natural gas, burned in industrial furnace >100kW	RER	MJ	1.42E+0	1	1.42	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		
	transport, lorry 32t	RER	tkm	1.08E-1	1	2.05	(4,na,na,na,na,na); standard distances		
	transport, freight, rail	RER	tkm	6.48E-1	1	2.05	(4,na,na,na,na,na); standard distances		
	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); estimation		
OUTPUTS	melamine formaldehyde resin, at plant	RER	kg	1.00E+0					
air emission	Heat, waste		MJ	4.68E-2	1	1.42	(3,5,3,3,3,5); calculated from electricity input		
	Formaldehyde		kg	1.00E-3	1	5.19	(3,5,3,3,3,5); data from survey in literature (von Däniken et al. 1995)		

89.9 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

89.10 Conclusions

Average European datasets for the production of the two resin forms for the year 2000 are established. These datasets are in accordance with the present quality guidelines of the ecoinvent project and are

both based on a report covering the European industry, based on statistics from the first half of the 1990s. The data are thus of a reasonable quality and can be used in quite a broad context.

89.11 EcoSpold Meta Information

ReferenceFunction	Name	<i>urea formaldehyde resin, with hardener, at plant</i>	<i>melamine formaldehyde resin, at plant</i>
Geography	Location	RER	RER
ReferenceFunction	InfrastructureProcess	0	0
ReferenceFunction	Unit	kg	kg
ReferenceFunction	LocalName	Harnstoff-Formaldehydharz,ab Werk	Melamin-Formaldehydharz,ab Werk
ReferenceFunction	Synonyms		
ReferenceFunction	GeneralComment	Manufacturing process is considered with consumption of raw materials, energy, infrastructure and land use, as well as the generation of emissions to air. Transportation of raw materials is also included. Auxiliaries, solid wastes and emissions to water are not included due to the lack of information. Transport and storage of the final product are not included. No byproducts or coproducts are considered. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Inventory refers to 1 kg 100% urea-formaldehyde resin. The literature source used are Diem 2000 and von Däniken et al. 1995.	Manufacturing process is considered with consumption of raw materials, energy, infrastructure and land use, as well as the generation of emissions to air. Transportation of raw materials is also included. Auxiliaries, solid wastes and emissions to water are not included due to the lack of information. Transport and storage of the final product are not included. No byproducts or coproducts are considered. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Inventory refers to 1 kg 100% urea-formaldehyde resin. The literature source used are Diem 2000 and von Däniken et al. 1995.
ReferenceFunction	CASNumber		
TimePeriod	StartDate	1995-12	1995-12
TimePeriod	EndDate	2000-12	1995-12
TimePeriod	DataValidForEntirePeriod	1	1
TimePeriod	OtherPeriodText	The literature sources are from 1995 and 2000. The time period to which the data presented in the sources corresponds is not known.	The literature sources are from 1995 and 2000. The time period to which the data presented in the sources corresponds is not known.
Geography	Text	For raw materials, data are taken from literature and refere to u-f resin. The other values are an approximation based on the manufacturing of alkyl resin. For this alkyl resin, data base on information provided by a European manufacturing company. Therefore, it is not known how representative are these values for the European urea-formaldehyde resin industry	For raw materials, data are taken from literature and refere to u-f resin. The other values are an approximation based on the manufacturing of alkyl resin. For this alkyl resin, data base on information provided by a European manufacturing company. It is not known how representative are these values for the European melamine-formaldehyde resin industry
Technology	Text	unknown	unknown
Representativeness	Percent		
Representativeness	ProductionVolume	unknown	unknown
Representativeness	SamplingProcedure	see OtherPeriodText	
Representativeness	Extrapolations	Transports based on standard distances of Ecoinvent. Infrastructure: proxy module used (chemical plant, organics)	Transports based on standard distances of Ecoinvent. Infrastructure: proxy module used (chemical plant, organics)
Representativeness	UncertaintyAdjustments	none	none

89.12 References

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90 Varnish materials

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90.1 Introduction

Within this report, materials for varnish compositions are described – in detail: acrylic binder, acrylic dispersion and acrylic varnish are shown.

90.2 Acrylic binder

This chapter corresponds to the module in the ecoinvent database: **Production of 1 kg acrylic binder, 54% in H₂O, at plant, in Europe. All data are referred to 1 kg acrylic binder 100%.**

The system includes the process with the consumption of energy, raw materials, infrastructure and land use as well as the generation of solid wastes and emissions into air and water. It also includes transportation of raw materials and wastes. Because of the lack of data on auxiliaries, no values can be presented and therefore, the transportation and consumption of auxiliaries are not included.

The system does also not include transportation of the final product acrylic binder. There are no by-products generated in the production process.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage is also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to hazardous waste incineration.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

90.2.1 Acrylic binder production process

Data source

For this study, data are taken from von Däniken *et al.* (1995), a survey from the Swiss Agency for the Environment, Forests and Landscape (BUWAL). The module used is “acrylic-binder, 46% in water” and bases on confidential data from European manufacturing companies.

Raw materials and auxiliaries

According von Däniken *et al.* (1995), 4.60 E-04 m³ water, 1.25 E-01 kg versatic acid, 7.40 E-02 kg butylacrylate and 2.70 E-01 kg vynilacetate are consumed for the manufacturing of 1 kg 100% acrylic binder. For ecoinvent database, the input of versatic acid is reported as “esters of versatic acid, at plant”, since this module is the most appropriate of the modules available.

Energy and transportation

von Däniken *et al.* (1995) presents values for consumption of electricity and termal energy. Based on the latter (1.20 MJ per kg binder), they calculate the consumption of different energy carriers.

The information regarding consumption of energy as presented in the mentioned source, is shown in Tab. 90.1.

Tab. 90.1 Consumption of energy in the production of acrylic binder

Input		(kg ⁻¹ 100% acrylic binder)
electricity	kWh	1.00 E-01
hardcoal	MJ	3.70 E-01
heavy fuel oil	MJ	2.20 E-01
light fuel oil	MJ	5.00 E-02
natural gas	MJ	5.50 E-01

In regard to transportation of raw materials and solid wastes, no information about distances is available in the examined data source. Therefore, for the raw materials, the following standard distances as defined in Frischknecht *et al.* (2003) were used: 100 km by lorry 32t and 600 km by train. Water is not included in the calculations. For the transportation of the different wastes produced within the process it is assumed that they are sent to landfill and, again, standard distances are used: 10 km by lorry to disposal site. Additionally, it is assumed that this lorry has a capacity of 32 tonnes in order to facilitate the calculations. Tab. 90.2 summarises the total transport amounts for the production of 1 kg of 100% acrylic binder.

Tab. 90.2 Total transport amounts and means for the production of acrylic binder.

(tkm. kg ⁻¹ 100% acrylic binder)	lorry	train
raw material	4.69 E-02	2.81 E-01
auxiliaries	Nd	nd
waste to disposal sites	3.00 E-04	0
Total transports	4.72 E-02	2.81 E-01

nd: no data available

Infrastructure and land use

There is no information available about infrastructure and land-use of acrylic binder plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. This estimated value is 4.00 E-10 unit. kg⁻¹ chemical.

Emissions to air and water

von Däniken *et al.* (1995) presents values for specific process emissions. Emissions arisen by the use of the different energy carriers are included in the corresponding modules and therefore are not further discussed here. Tab. 90.3 shows the information concerning process emissions into air and into water, as presented in the mentioned source.

Tab. 90.3 Process emissions to air and water from the production process of acrylic binder (Taken from von Däniken et al. (1995))

Process emissions ¹	Value (kg ⁻¹ 100% acrylic binder)	
Emissions to air		
Hydrocarbons	kg	7.00 E-05
Emissions to water		
BOD	kg	1.80 E-05
COD	kg	1.70 E-04
Dissolved solids	kg	3.60 E-04
Suspended solids	kg	2.10 E-05
Total Organic Carbon	kg	4.00 E-05
Dissolved Organic Carbon	kg	1.10 E-05

¹: Emissions corresponding to the use of energy carriers are not included.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. Basing on this assumption the necessary conversion from kWh to MJ is done according to Frischknecht *et al.* (2003). Thus, considering the energy input of 1.00 E-01 kWh, the value of waste-heat taken for this study is 3.60 E-01 MJ.kg⁻¹ binder.

Emission to air of unspecified hydrocarbons is reported as "Hydrocarbons, aliphatic, alkanes, unspecified" since this is most approximated module available in ecoinvent database.

Wastes

von Däniken *et al.* (1995) mentions the generation of 3.00 E-02 kg solid waste per kg binder manufactured. No further information about the solid waste and its disposition is available. For this study, waste is reported as "disposal, paint remains, 0 %water, to hazardous waste incineration". This is considered the most appropriate among the different modules available in the database.

90.2.2 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

von Däniken *et al.* (1995) base their data on information provided by European manufacturing companies, but unfortunately there is no further information about the number of companies involved in the study, if data are based on reports, estimations, etc. Therefore, it is difficult to assess the representativeness of the data.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht *et al.* (2003) (transport) resp. the very general module of an organic chemical plant are used.

Tab. 90.4 summarises the input and output data as well as the uncertainties used for the production of acrylic binder. The values are given for the production of 1 kg of 100% acrylic binder. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 90.7.

Tab. 90.4 Input- / Output-data for the production of acrylic binder (expressed per kg 100% acrylic binder produced)

Explanation	Name	Location	Unit	acrylic binder, 54% in H ₂ O, at plant			GeneralComment
				RER	UncertaintyType	StandardDeviation	
				0 kg	95%		
Resources Input from Technosphere	Water, unspecified natural origin	m3	4.60E-4	1	1.65	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	butyl acrylate, at plant	RER	kg	7.40E-2	1	1.65	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)
	vinyl acetate, at plant	RER	kg	2.70E-1	1	1.65	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)
	esters of versatic acid, at plant	RER	kg	1.25E-1	1	1.65	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	1.00E-1	1	1.65	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)
	hard coal, burned in industrial furnace 1-10MW	RER	MJ	3.70E-1	1	1.65	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)
	heat, heavy fuel oil, at industrial furnace 1MW	RER	MJ	2.20E-1	1	1.65	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)
	heat, light fuel oil, at industrial furnace 1MW	RER	MJ	5.00E-2	1	1.65	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)
	natural gas, burned in industrial furnace >100kW	RER	MJ	5.50E-1	1	1.65	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)
	transport, lorry 32t	RER	tkm	4.72E-2	1	2.05	(4,na,na,na,na,na); standard distances
	transport, freight, rail	RER	tkm	2.81E-1	1	2.05	(4,na,na,na,na,na); standard distances
	chemical plant, organics	RER	unit	4.00E-10	1	3.98	(4,1,5,3,5,4); estimation
waste	disposal, paint remains, 0% water, to hazardous waste incineration	CH	kg	3.00E-2	1	2.29	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)
Output air emission	acrylic binder, 54% in H ₂ O, at plant	RER	kg	1.00E+0			
water emission	Heat, waste	MJ	3.60E-1	1	1.65	(3,5,5,3,1,5); calculated from electricity input	
	Hydrocarbons, aliphatic, alkanes, unspecified	kg	7.00E-5	1	2.12	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	BOD ₅ , Biological Oxygen Demand	kg	1.80E-5	1	1.90	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	COD, Chemical Oxygen Demand	kg	1.70E-4	1	1.90	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	Solved solids	kg	3.60E-4	1	1.90	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	Suspended solids, unspecified	kg	2.10E-5	1	1.90	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	TOC, Total Organic Carbon	kg	4.00E-5	1	1.90	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	DOC, Dissolved Organic Carbon	kg	1.10E-5	1	1.90	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	

90.3 Acrylic dispersion

This chapter corresponds to the module in the ecoinvent database: **Production of 1 kg acrylic dispersion, 34% in H₂O, at plant, in Europe. Nevertheless, all data are referred to 1 kg 100% base for acrylic dispersion.**

The system includes the process with the consumption of raw materials, energy, infrastructure and land use as well as the generation of solid wastes and the emissions into air of heat waste. It also includes transportation of raw materials and wastes. No other emissions into air or into water are considered due to the lack of data. Auxiliaries are also not included because of lack of information.

The system does also not include transportation of the final product acrylic dispersion. There are no by-products generated in the production process.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage is also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. Solid wastes are assumed to be sent to hazardous waste incineration.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air.

90.3.1 Acrylic dispersion production process

Data source

For this study, data are taken from SZFF (1996), an environmental assessment of windows from the Swiss and the Swiss Federal Laboratories for Materials Testing and Research (EMPA). They base on information provided by SIGMA Coatings BV. Numbers for three bases for acrylic dispersion are presented.

Raw materials and auxiliaries

Tab. 90.5 shows the consumption of raw materials in the production of the different bases for acrylic dispersion, according the source consulted, as well as the average used in this study. There is no data available on the consumption of auxiliaries.

Tab. 90.5 Consumption of raw materials in the production of different bases for acrylic dispersion.

Raw material (per kg 100% base manufac- tured)	unit	Thick layer lacquer	intermediate and top- coat lacquer	primer and top-coat paint	AVERAGE base This study
water	m ³	1.96 E-04	1.78 E-04	1.78 E-04	1.84 E-04
Acrylic binder	kg	5.02 E-01	5.22 E-01	4.86 E-01	5.03 E-01
Titanium diox- ide (from chlo- ride process)	kg	2.40 E-01	2.40 E-01	2.73 E-01	2.51 E-01
Ethylene glycol	kg	4.00 E-02	4.00 E-02	4.00 E-02	4.00 E-02
Chemicals, or- ganics, un- specified	kg	5.00 E-03	5.00 E-03	5.00 E-03	5.00 E-03
Butyl acrylate	kg	1.00 E-02	1.00 E-02	1.00 E-02	1.00 E-02
Butanol	kg	5.15 E-03	5.15 E-03	5.15 E-03	5.15 E-03

Energy and transportation

According the source consulted, the manufacture of 1 kg base for acrylic dispersion requires an electricity input of 1.08 MJ (0.3 kWh).

In regard to transportation of raw materials or solid wastes, no information about distances is available in the examined data source. Therefore, for the raw materials, the following standard distances as defined in Frischknecht *et al.* (2003) were used: 100 km by lorry 32t and 600 km by train. Water is not included in the calculations. For the transportation of the different wastes produced within the process it is assumed that they are sent to landfill and, again, standard distances are used: 10 km by lorry to disposal site. Additionally, it is assumed that this lorry has a capacity of 32 tonnes in order to facilitate the calculations. Tab. 90.6 summarises the total transport amounts for the production of 1 kg of 100% acrylic dispersion.

Tab. 90.6 Total transport amounts and means for the production of acrylic dispersion.

(tkm. kg ⁻¹ 100% base for acrylic dispersion)	lorry	train
raw material	8.45 E-02	5.07 E-01
auxiliaries	nd	nd
waste to disposal sites	1.60 E-06	0
Total transports	8.45 E-02	5.07 E-01

nd: no data available

Infrastructure and land use

There is no information available about infrastructure and land-use of acrylic dispersion plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. This estimated value is 4.00 E-10 unit. kg⁻¹ chemical.

Emissions to air and water

The source consulted does not present any numbers for emissions into air and water.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. This means that 1.08 MJ waste-heat arise by the manufacturing process.

Wastes

The production of 1 kg base for acrylic dispersion generates 1.60 E-03 kg solid waste. No further information about the solid waste and its disposition is available. For this study, waste is reported as "disposal, emulsion paint remains, 0 %water, to hazardous waste incineration". This is considered the most appropriate among the different modules available in the database.

90.3.2 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

Data in the SZFF 1996 base on information provided by the above mentioned manufacturing company, but unfortunately there is no further information about these data and therefore, it is difficult to assess their representativeness.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht *et al.* 2003 (transport) resp. the very general module of an organic chemical plant are used.

Tab. 90.7 summarises the input and output data as well as the uncertainties used for the production of acrylic dispersion. The values are given for the production of 1 kg of 100% base for acrylic dispersion. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 90.7.

Tab. 90.7 Input- / Output-data for the production of acrylic dispersion (expressed per kg 100% acrylic dispersion produced)

Explanation	Name	Location	Unit	acrylic dispersion, 65% in H ₂ O, at plant		Uncertainty Type	Standard deviation 95%	General Comment
				RER	kg			
				Infrastructure	Process			
Resources input from Technosphere	Water, unspecified natural origin		m ³	1.84E-4	1	1.34	(3,5,3,3,1,5); data from survey in literature (SFZ 1996)	
	acrylic binder, 54% in H ₂ O, at plant	RER	kg	5.03E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (SFZ 1996)	
	titanium dioxide, chloride process, at plant	RER	kg	2.51E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (SFZ 1996)	
	ethylene glycol, at plant	RER	kg	4.00E-2	1	1.34	(3,5,3,3,1,5); data from survey in literature (SFZ 1996)	
	butyl acrylate, at plant	RER	kg	1.00E-2	1	1.34	(3,5,3,3,1,5); data from survey in literature (SFZ 1996)	
	chemicals organic, at plant	GLO	kg	5.00E-3	1	1.34	(3,5,3,3,1,5); data from survey in literature (SFZ 1996)	
	butanol, 1-, at plant	RER	kg	5.15E-3	1	1.34	(3,5,3,3,1,5); data from survey in literature (SFZ 1996)	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.00E-1	1	1.34	(3,5,3,3,1,5); data from survey in literature (SFZ 1996)	
	transport, lorry 32t	RER	tkm	8.45E-2	1	2.05	(4,na,na,na,na,na); standard distances	
	transport, freight, rail	RER	tkm	5.07E-1	1	2.05	(4,na,na,na,na,na); standard distances	
Outputs	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); estimation	
	disposal, emulsion paint remains, 0% water, to hazardous waste incineration	CH	kg	1.63E-3	1	1.34	(3,5,3,3,1,5); data from survey in literature (SFZ 1996)	
air emission	acrylic dispersion, 65% in H ₂ O, at plant	RER	kg	1.00E+0				
	Heat, waste		MJ	1.08E+0	1	1.34	(3,5,3,3,1,5); calculated from electricity input	

90.4 Acrylic varnish

This report corresponds to the module in the ecoinvent database for the **production of 1 kg acrylic varnish, 87.5% in H₂O, at plant, in Europe. All data are referred to 1 kg acrylic varnish 100%.**

The system includes the process with raw materials, auxiliaries, infrastructure and land use, transportation of the raw materials and wastes as well as the generation of solid wastes and emissions to air and water. It does not include transportation of the final product acrylic varnish. There are no by-products generated in the production process.

For the study transient or unstable operations like starting-up or shutting-down, are not included, but the production during stable operation conditions. Storage is also not included.

It is assumed that the manufacturing plants are located in an urban/industrial area and consequently the emissions are categorised as emanating in a high population density area. The emissions into water are assumed to be emitted into rivers.

It is assumed that 100% of the electricity consumed is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.

90.4.1 Acrylic varnish production process

Data sources

The data source for this study is von Däniken *et al.* (1995), a survey from the Swiss Agency for the Environment, Forests and Landscape (BUWAL) where an environmental assessment of this varnish is performed. The source of the data is not presented.

Raw materials and auxiliaries

According to von Däniken *et al.* (1995), for the manufacturing of 1 kg acrylic varnish the following raw materials are required:

- 5.00 E-01 kg acrylic binder
- 1.25 E-03 kg ammonia
- 5.00 E-02 kg ethylenglicol
- 2.00 E-01 kg titanium dioxide (manufactured by the chloride process) and
- 2.35 E-04 m³ water

Energy and transportation

According to the source mentioned, an electricity input of 1.08 MJ is consumed for the manufacturing of 1 kg acrylic varnish. Since electricity is reported in kWh in ecoinvent database, the necessary conversion is done according to Frischknecht *et al.* (2003). Thus, the value reported is 3.00 E-01 kWh per kg varnish manufactured.

In regard to transportation of raw materials, no information about distances is available in the examined data source. Therefore, standard distances as defined in Frischknecht *et al.* (2003) were used: 100 km by lorry 32t and 600 km by train. Water is not included in the calculations. For auxiliaries and solid wastes no estimation of transport amounts can be made because there are even no values for consumption of auxiliaries or generation of wastes. Tab. 90.8 summarises the total transport amounts for the production of 1 kg of 100% acrylic varnish.

Tab. 90.8 Total transport amounts and means for the production of acrylic varnish.

(tkm. kg ⁻¹ 100% acrylic varnish)	lorry	train
raw material	7.50 E-02	4.50 E-01
auxiliaries	nd	nd
waste to disposal sites	nd	nd
Total transports	7.50 E-02	4.50 E-01

nd: no data available

Infrastructure and land use

There is no information available about infrastructure and land-use of varnish plants. Therefore, in this study, the infrastructure is estimated based on the module "chemical plant, organics", that has a built area of about 4.2 ha and an average output of 50'000 t/a. For more details about this infrastructure module, see chapter 2.7 in part I of this report. Thus, for this study, the estimated value is 4.00 E-10 unit. kg⁻¹ acrylic varnish.

Solid wastes and emissions to air and water

The source used does not present any numbers for solid wastes or emissions to air and water.

For ecoinvent database, it is assumed that 100% of the electricity consumed is converted to waste heat and that 100% of the waste heat is released to the air. Basing on this assumption, a waste-heat of 1.08 E+00 MJ.kg⁻¹ varnish is reported.

90.4.2 Data quality considerations

The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

There is no background information about the data presented in von Däniken *et al.* 1995. This leads to high uncertainty scores.

The transport and infrastructure data are two further areas with much higher uncertainties. Due to a complete lack of data, assumptions based on Frischknecht *et al.* 2003 (transport) resp. the very general module of an organic chemical plant are used.

Tab. 90.9 summarises the input and output data as well as the uncertainties used for the production of acrylic varnish. The values are given for the production of 1 kg of 100% acrylic varnish. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 90.7.

Tab. 90.9 Input- / Output-data for the production of acrylic varnish (expressed per kg 100% acrylic varnish produced)

Explanation	Name	Location	Unit	acrylic varnish, 87.5% in H ₂ O, at plant		UncertaintyType	StandardDeviation95%	GeneralComment
				RER	0 kg			
				Infrastructure	Process			
Resources Input from Technosphere	Water, unspecified natural origin		m3	2.35E-4	1	1.64	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	acrylic binder, 54% in H ₂ O, at plant	RER	kg	5.00E-1	1	1.64	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	ammonia, liquid, at regional storehouse	RER	kg	1.25E-3	1	1.64	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	ethylene glycol, at plant	RER	kg	5.00E-2	1	1.64	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	titanium dioxide, chloride process, at plant	RER	kg	2.00E-1	1	1.64	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.00E-1	1	1.64	(3,5,5,3,1,5); data from survey in literature (von Däniken et al. 1995)	
	transport, lorry 32t	RER	tkm	7.50E-2	1	2.05	(4,na,na,na,na,na); standard distances	
	transport, freight, rail	RER	tkm	4.50E-1	1	2.05	(4,na,na,na,na,na); standard distances	
OUTPUTS	chemical plant, organics	RER	unit	4.00E-10	1	3.96	(4,1,5,3,5,4); estimation	
air emission	acrylic varnish, 87.5% in H ₂ O, at plant	RER	kg	1.00E+0				
	Heat, waste		MJ	1.08E+0	1	1.64	(3,5,5,3,1,5); calculated from electricity input	

90.5 Cumulative Results and Interpretation

Results of the cumulative inventories can be downloaded from the database.

90.6 Conclusions

Average European datasets for the production of the different acrylic products for the year 2000 are established. The datasets are in accordance with the present quality guidelines of the ecoinvent project and are based on a report covering the European industry, based on statistics from the first half of the 1990s. The data are thus of a reasonable quality and it should be possible to use them in quite a broad context.

90.7 EcoSpold Meta Information

ReferenceFunction	Name	acrylic binder, 54% in H2O, at plant	acrylic dispersion, 65% in H2O, at plant	acrylic varnish, 87.5% in H2O, at plant
Geography	Location	RER	RER	RER
ReferenceFunction	InfrastructureProcess	0	0	0
ReferenceFunction	Unit	kg	kg	kg
ReferenceFunction	IncludedProcesses			
ReferenceFunction	Amount	1	1	1
ReferenceFunction	LocalName	Acrylat-Bindemittel, 54% in H2O, ab Werk	Acryl-Dispersion, 65% in H2O, ab Werk	Acryl-Lack, 87.5% in H2O, ab Werk
ReferenceFunction	Synonyms			
ReferenceFunction	GeneralComment	<p>Manufacturing process is considered with consumption of raw materials, energy, infrastructure and land use, as well as generation of solid wastes and emissions into air and water. Transport of the raw materials and solid wastes is included. No by-product is generated in the process. Transportation and consumption of auxiliaries are not included due to the lack of data.</p> <p>Transport and storage of the final product are not included. Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to hazardous waste incineration. Inventory refers to 1 kg 100% acrylic binder. The literature source is von Däniken et al. 1995.</p>	<p>Manufacturing process is considered with consumption of raw materials, energy, infrastructure and land use, as well as generation of solid wastes and emissions into air of heat waste. No other emissions into air or into water are included, due to lack of data.</p> <p>Transport of the raw materials and solid wastes is included. No by-product is generated in the process.</p> <p>Transportation and consumption of auxiliaries are not included due to the lack of data. Transport and storage of the final product are not included.</p> <p>Transient or unstable operations are not considered, but the production during stable operation conditions. Emissions to air are considered as emanating in a high population density area. Emissions into water are assumed to be emitted into rivers. Solid wastes are assumed to be sent to hazardous waste incineration. Inventory refers to 1 kg 100% base for acrylic dispersion binder. The literature source is SZFF 1996</p>	<p>Manufacturing process is considered with consumption of raw materials, energy, as well as infrastructure and land use. Transport of the raw materials is included. No by-product is generated in the process. Auxiliaries, solid wastes and emissions to air and water (excepting emission of waste-heat) are not included due to the lack of data.</p> <p>Transport and storage of the final product are not included. Transient or unstable operations are not considered, but the production during stable operation conditions. Inventory refers to 1 kg 100% acrylic varnish. The literature source used is von Däniken et al. 1995</p>
ReferenceFunction	CASNumber			
TimePeriod	StartDate	1995-12	1996-12	1995-12
TimePeriod	EndDate	1995-12	1996-12	1995-12
TimePeriod	DataValidForEntirePeriod	1	1	1
TimePeriod	OtherPeriodText	literature bases on data from the 1990s.		
Geography	Text	The literature source used bases on information provided by European manufacturing companies. No further information is available on the location and characteristics of these manufacturers. Therefore, the representativeness of these values for the European acrylic binder industry is unknown.	The literature source used bases on information provided by SIGMA Coatings BV. The representativeness of these values for the European acrylic binder industry is unknown.	The literature source used bases on information provided by manufacturing companies. No further information is available on the location and characteristics of these manufacturers. Therefore, the representativeness of these values for the European acrylic varnish industry is unknown.
Technology	Text	unknown	unknown	unknown
Representativeness	Percent			
Representativeness	ProductionVolume	unknown	unknown	unknown
Representativeness	SamplingProcedure	see geography	see geography	see geography
Representativeness	Extrapolations	Transports based on standard distances of EcoInvent. Infrastructure: proxy module used (chemical plant, organics)	Transports based on standard distances of EcoInvent. Infrastructure: proxy module used (chemical plant, organics)	Transports based on standard distances of EcoInvent. Infrastructure: proxy module used (chemical plant, organics)
Representativeness	UncertaintyAdjustments	none	none	none

90.8 References

Frischknecht et al. 2003

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91 Versatic acid vinyl ester (VeoVa)

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91.1 Introduction

This chapter describes the production of VeoVa-10, also known as vinyl neodecanoate, CAS-nr 51000-52-3. This chemical is used primarily for the production of emulsion paints, as well as acrylic coatings.

91.2 Reserves and resources of VeoVa-10

VeoVa-10 is an organic chemical containing ten carbon atoms, hence the name VeoVa-10.. It is the vinyl ester of versatic 10, a synthetic, highly branched acid also known as neodacenoic acid.

91.3 Characterisation of Versatic 10 and Veova-10

Versatic 10 is a clear liquid with a melting point of < 30 °C. and a boiling range of 270 – 280 °C. It is not miscible with water but is completely miscible with vinyl acetate.

VeoVa-10, C₁₂H₂₂O₂, is a mobile liquid monomer with a boiling point 133-136 °C. VeoVa-10 is not readily biodegradable. Veova-10 is very toxic to freshwater fish and may cause long-term adverse effects in the aquatic environment. However, risks to human health and to the environment were not yet quantified at the time of writing (early 2003).

91.4 Production and use of Veova-10

VeoVa-10 is used as a co-monomer to react with other substances, producing a latex polymer dispersion. The latices are then used in the production of waterborne decorative paints (aka emulsion paints). There is also some production as a waterborne industrial adhesive. Latices based on VeoVa when used in waterborne decorative paints and coatings, are said to provide superior properties vis-à-vis “standard” paints:

- higher scrub and washability resistance
- improved weather resistance in exterior-use products
- alkali resistant when used on bricks and masonry

No production information is readily available.

91.5 System characterization

Veova-10 is produced industrially by reacting Veersatic-10 with acetylene. There are no competing routes for the production of Veova-10. Production information is strictly confidential.

91.6 Data quality considerations

The production information available stems from the producer and is relatively detailed. It may however not be reproduced publicly, which is why only the cumulative results are presented in this report. The fuels and boiler data are taken from refinery inventories that are part of the Ecoinvent data collection. No air monitoring information has been made available, so there was no input of process emissions, only fuel-based emissions are accounted for.

91.7 Cumulative Results and Interpretation

Results of the cumulative inventory can be downloaded from the database.

92 Water

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Last update 2003 (with correction of errors in 2007)

Acknowledgement

We thank Olivier Jolliet for the information provided in a personal communication.

92.1 Introduction

This chapter investigates the provision of drinking water in Europe and Switzerland.

92.2 Reserves and Resources

Drinking water can be produced from springs, groundwater, lakes, rivers and desalting of salt water. About half of the drinking water in Switzerland needs no specific treatment. About 5% of the available resources are used in the moment as drinking water in Switzerland. In Europe the average is 11% and thus much higher (BFS 2002).

92.3 Use of Water

Water is used by households, public services, and industry. The average consumption in Switzerland is 400 litres per person and day. This equals about 1 billion m³ per year (BFS 2002).

92.4 System Characterisation

The drinking water system includes the supply network, intermediate storage facilities, pump stations, and the water works itself. Drinking water can be treated by flocculation, fast and slow filters, oxidation, and active carbon. For this report a plant in Switzerland is investigated as an example.

92.5 Life Cycle Inventory for Drinking Water

The life cycle inventory for water treatment is based on a detailed study by (Crettaz 2000; Crettaz et al. 1998; Jolliet et al. 2000).

92.5.1 Infrastructure

Tab. 92.1 shows the unit process data for the infrastructure. Most of the data have been directly taken from an analysis of a drinking water supply in Marin (NE) in Switzerland (Crettaz et al. 1998). Own assumptions have been used for transports of materials, energy use for construction works, and disposal of materials. Doka (2003) has investigated data for the energy uses during construction of sewer networks that is used here as a proxy for the supply network. Land use for this network is not considered as the pipelines are mainly underground. Land use for other facilities has been estimated roughly.

The life time of the installations is normalized to 70 years. The annual capacities can be found in the last row of Tab. 92.1.

Tab. 92.1 Unit process raw data and data quality indicators for drinking water infrastructure in Switzerland (Crettaz et al. 1998)

	Name	Location	Infrastructure	Unit	water supply network				Uncertainty Standard Deviations 95	General Comment
					CH	CH	CH	CH		
					1 km	1 unit	1 unit	1 unit		
resource	Occupation, industrial area	-	-	m2a	0	4.38E+4	1.75E+5	7.00E+5	1 1.77	(5,na,1,1,1,na); Rough estimation for 70a life time
	Transformation, from unknown	-	-	m2	0	6.25E+2	2.50E+3	1.00E+4	1 2.23	(5,na,1,1,1,na); Rough estimation
	Transformation, to industrial area	-	-	m2	0	6.25E+2	2.50E+3	1.00E+4	1 2.23	(5,na,1,1,1,na); Rough estimation
technosphere	cast iron, at plant	RER	0	kg	2.13E+4	4.49E+3	0	1.82E+4	1 1.22	(2,3,1,1,1,5); Literature
	pig iron, at plant	GLO	0	kg	0	0	0	5.10E+2	1 1.22	(2,3,1,1,1,5); Literature
	brass, at plant	CH	0	kg	2.18E+0	6.30E-1	0	1.90E+0	1 1.22	(2,3,1,1,1,5); Literature
	bronze, at plant	CH	0	kg	0	1.05E+0	0	3.20E+0	1 1.22	(2,3,1,1,1,5); Literature
	aluminium, production mix, at plant	RER	0	kg	0	1.10E+1	0	1.12E+1	1 1.22	(2,3,1,1,1,5); Literature
	chromium steel 18/8, at plant	RER	0	kg	1.23E+1	0	0	0	1 1.22	(2,3,1,1,1,5); Literature
	reinforcing steel, at plant	RER	0	kg	0	1.80E+4	6.27E+4	8.11E+4	1 1.22	(2,3,1,1,1,5); Literature
	steel, low-alloyed, at plant	RER	0	kg	0	3.22E+3	4.54E+3	2.55E+4	1 1.22	(2,3,1,1,1,5); Literature
	copper, at regional storage	RER	0	kg	0	8.61E+2	0	2.75E+3	1 1.22	(2,3,1,1,1,5); Literature
	zinc, primary, at regional storage	RER	0	kg	1.47E+2	0	0	1.02E+3	1 1.22	(2,3,1,1,1,5); Literature
	bitumen sealing, at plant	RER	0	kg	5.35E+2	0	0	0	1 1.22	(2,3,1,1,1,5); Literature
	synthetic rubber, at plant	RER	0	kg	3.31E+1	4.20E-1	0	1.30E+0	1 1.22	(2,3,1,1,1,5); Literature
	polyvinylchloride, bulk polymerised, at plant	RER	0	kg	0	1.16E+3	0	2.56E+3	1 1.22	(2,3,1,1,1,5); Literature
	polyurethane, rigid foam, at plant	RER	0	kg	5.35E+2	0	0	0	1 1.22	(2,3,1,1,1,5); Literature
	tetrafluoroethylene, at plant	RER	0	kg	5.94E-2	0	0	0	1 1.22	(2,3,1,1,1,5); Literature
	flat glass, coated, at plant	RER	0	kg	0	3.23E+2	0	2.84E+1	1 1.22	(2,3,1,1,1,5); Literature
	cement, unspecified, at plant	CH	0	kg	0	5.28E+4	0	0	1 1.22	(2,3,1,1,1,5); Literature
	brick, at plant	RER	0	kg	0	0	0	1.35E+5	1 1.22	(2,3,1,1,1,5); Literature
	silica sand, at plant	DE	0	kg	0	0	0	2.09E+5	1 1.22	(2,3,1,1,1,5); Literature
	expanded vermiculite, at plant	CH	0	kg	0	0	0	1.44E+4	1 1.22	(2,3,1,1,1,5); Literature
	concrete, normal, at plant	CH	0	m3	0	2.27E+2	7.03E+2	1.17E+4	1 1.22	(2,3,1,1,1,5); Literature
	poor concrete, at plant	CH	0	m3	0	1.61E+1	2.93E+1	0	1 1.22	(2,3,1,1,1,5); Literature
	excavation, hydraulic digger	RER	0	m3	5.45E+3	0	0	0	1 1.41	(3,5,3,1,3,5); Rough estimation with data for class 3 sewer system
	diesel, burned in building machine	GLO	0	MJ	2.94E+4	0	0	0	1 1.41	(3,5,3,1,3,5); Rough estimation with data for class 3 sewer system
	transport, lorry 20-28t, fleet average	CH	0	tkm	1.13E+3	1.48E+4	3.56E+4	5.38E+5	1 2.09	(4,5,na,na,na,na); Standard distance 50km
	transport, freight, rail	CH	0	tkm	1.35E+4	4.85E+4	4.03E+4	2.94E+5	1 2.09	(4,5,na,na,na,na); Standard distance 600km
	disposal, building, bitumen sheet, to final disposal	CH	0	kg	5.35E+2	0	0	0	1 1.22	(2,3,1,1,1,5); Estimation for materials used
	disposal, polyurethane, 0.2% water, to municipal incineration	CH	0	kg	5.35E+2	0	0	0	1 1.22	(2,3,1,1,1,5); Estimation for materials used
	disposal, building, reinforced concrete, to sorting plant	CH	0	kg	0	5.36E+5	1.61E+6	2.57E+7	1 1.22	(2,3,1,1,1,5); Estimation for materials used
	disposal, polyvinylchloride, 0.2% water, to municipal incineration	CH	0	kg	0	1.16E+3	0	2.56E+3	1 1.22	(2,3,1,1,1,5); Estimation for materials used
	disposal, rubber, unspecified, 0% water, to municipal incineration	CH	0	kg	3.31E+1	4.20E-1	0	1.30E+0	1 1.22	(2,3,1,1,1,5); Estimation for materials used
	disposal, plastics, mixture, 15.3% water, to municipal incineration	CH	0	kg	5.94E-2	0	0	0	1 1.22	(2,3,1,1,1,5); Estimation for materials used
	disposal, building, glass pane (in burnable frame), to final disposal	CH	0	kg	0	3.23E+2	0	2.84E+1	1 1.22	(2,3,1,1,1,5); Estimation for materials used
	disposal, building, reinforcement steel, to sorting plant	CH	0	kg	2.13E+4	4.49E+3	0	1.82E+4	1 1.22	(2,3,1,1,1,5); Estimation for materials used
	disposal, building, cement (in concrete) and mortar, to sorting plant	CH	0	kg	0	5.28E+4	0	3.58E+5	1 1.22	(2,3,1,1,1,5); Estimation for materials used
life time capacity				a	70	70	70	70		
				m3/70a	4.86E+7	4.86E+7	4.86E+7	8.40E+7		

92.5.2 Treatment

Tab. 92.2 shows the unit process raw data for the treatment of drinking water. The data have been investigated in a case study in Switzerland (Crettaz et al. 1998). Further data were available from a German study (Ebersperger 1995). They are extrapolated here for the European situation. The average electricity consumption for Switzerland and Germany is used. It might show large variation depending on the treatment options used. The use of water resources has been estimated based on the distribution in Switzerland (BFS 2002). The efficiency of water uptake to delivery is estimated at 95%. Information for the emissions due to use of chemicals was not available. A part will be disposed with sludge while another part goes to the effluents. It is estimated that the whole amount of chemicals is emitted to rivers, because these substances are normally not well removed in a waste water treatment plant.

Tab. 92.2 Unit process raw data and data quality indicators for drinking water in Switzerland and Europe (Crettaz et al. 1998; Ebersperger 1995)

	Name	Location	Infrastructure	Unit	tap water, at user	tap water, at user	Uncertainty standard deviations %	General Comment	tap	tap	tap
					RER	CH			water, at user	water, at user	water, at user
					kg	kg			kg	kg	kg
product	tap water, at user	RER	0	kg	1.00E+0	0			CH	DE	CH
	tap water, at tap	CH	0	kg	0	1.00E+0			0	0	0
resource, in water	Water, river	-	-	m3	4.78E-4	4.78E-4	1	1.07 (1,3,1,3,1,1); Literature for CH, efficiency 95%			
	Water, lake	-	-	m3	1.91E-4	1.91E-4	1	1.07 (1,3,1,3,1,1); Literature for CH, efficiency 95%			
	Water, well, in ground	-	-	m3	3.83E-4	3.83E-4	1	1.07 (1,3,1,3,1,1); Literature for CH, efficiency 95%			
technosphere	electricity, medium voltage, production										
	UCTE, at grid	UCTE	0	kWh	3.90E-4	0	1	4.00 Average for Germany and deviation found in CH	3.77E-4	3.90E-4	
	electricity, medium voltage, at grid	CH	0	kWh	0	3.90E-4	1	4.00 Average for Switzerland and deviation found in the country.			4.10E-4
	chlorine, liquid, production mix, at plant	RER	0	kg	1.00E-7	1.00E-7	1	1.22 (2,3,1,3,1,5); Literature	4.00E-8	1.00E-7	
	hydrogen peroxide, 50% in H ₂ O, at	RER	0	kg	8.80E-7	8.80E-7	1	1.22 (2,3,1,3,1,5); Literature		8.80E-7	
	ozone, liquid, at plant	RER	0	kg	3.33E-6	3.33E-6	1	1.22 (2,3,1,3,1,5); Literature		3.33E-6	
	charcoal, at plant	GLO	0	kg	4.17E-6	4.17E-6	1	1.22 (2,3,1,3,1,5); Literature		4.17E-6	
	aluminium sulphate, powder, at plant	RER	0	kg	6.33E-6	6.33E-6	1	1.22 (2,3,1,3,1,5); Literature, approximation for WAC (aluminium polychlorid)			6.33E-6
	water supply network	CH	1	km	3.14E-10	3.14E-10	1	3.05 (2,3,1,3,1,5); Average for Switzerland			
	pump station	CH	1	unit	2.06E-11	2.06E-11	1	3.05 (2,3,1,3,1,5); Literature			
	water storage	CH	1	unit	2.06E-11	2.06E-11	1	3.05 (2,3,1,3,1,5); Literature			
	water works	CH	1	unit	1.19E-11	1.19E-11	1	3.05 (2,3,1,3,1,5); Literature			
	disposal, wood untreated, 20% water, to										
	municipal incineration	CH	0	kg	4.17E-6	4.17E-6	1	1.22 (2,3,1,3,1,5); charcoal disposal			
	treatment, sewage, unpolluted, to										
	wastewater treatment, class 3	CH	0	m3	5.00E-5	5.00E-5	1	1.57 (5,3,1,3,1,5); Rough estimation for efficiency			
	transport, freight, rail	RER	0	tkm	8.89E-6	8.89E-6	1	2.09 (4,5,na,na,na,na); Standard distance 600km			
	transport, lorry 32t	RER	0	tkm	1.48E-6	1.48E-6	1	2.09 (4,5,na,na,na,na); Standard distance 100km			
emission air, high population density	Heat, waste	-	-	MJ	1.40E-3	1.40E-3	1	1.22 (2,3,1,1,1,5); Literature			
emission water,	Aluminum	-	-	kg	1.29E-6	1.29E-6	1	1.77 (5,na,1,1,1,na); Estimation for chemical (WAC)			
	Chlorine	-	-	kg	1.00E-7	1.00E-7	1	1.77 (5,na,1,1,1,na); Estimation for chemical (Cl2) use			
	Chloride	-	-	kg	5.04E-6	5.04E-6	1	1.77 (5,na,1,1,1,na); Estimation for chemical (WAC)			
efficiency					95%	95%					
source									www.n (Ebers euweile perger1 rag.ch 995) (Cretta z et al. 1998)		

92.5.3 Decarbonisation and Deionisation

Decarbonisation and deionisation of water for the use in power plants is investigated for this project in another report (Jungbluth 2003).

92.6 Cumulative Results and Interpretation

Cumulative results can be downloaded from the database (www.ecoinvent.ch).

Appendices: EcoSpold Meta Information

	401 Name	tap water, at user	tap water, at user	water supply network	pump station	water storage	water works
ReferenceFunction	402 Location	RER	CH	CH	CH	CH	CH
Geography	403 InfrastructureProcess	0	0	1	1	1	1
ReferenceFunction	403 Unit	kg	kg	km	unit	unit	unit
DataSetInformation	201 Type	1	1	1	1	1	1
	202 Version	1.0	1.0	1.0	1.0	1.0	1.0
	203 energyValues	0	0	0	0	0	0
	205 LanguageCode	en	en	en	en	en	en
	206 LocalLanguageCode	de	de	de	de	de	de
DataEntryBy	302 Person	41	41	41	41	41	41
	304 QualityNetwork	1	1	1	1	1	1
ReferenceFunction	400 DataSetRelatesToProduct	1	1	1	1	1	1
	402 IncludedProcesses	Infrastructure and energy use for water treatment and transportation to the end user. No emissions from water treatment.		Infrastructure and energy use for water treatment and transportation to the end user. No emissions from water treatment.		Materials, transports, disposal for the infrastructure. Estimation for building process. No land use for construction work.	
	404 Amount	1	1	1	1	1	1
	490 LocalName	Trinkwasser, ab Hausanschluss	Trinkwasser, ab Hausanschluss	Trinkwassernetz	Pumpstation	Trinkwasserspeicher	Wasserwerk
	491 Synonyms						
	492 GeneralComment	Rough estimation investigated for CH and data for energy use in DE.		About 712 Mio m ³ per year are transported in the Swiss water supply network. Life time 70 years.		Estimation for a pump station in Marin (NE) with a capacity of 644546 m ³ per year. Life time 70 years.	
	494 InfrastructureIncluded	1	1				
	495 Category	water supply	water supply	water supply	water supply	water supply	water supply
	496 SubCategory	production	production	production	production	production	production
	497 LocalCategory	Wasserversorgung	Wasserversorgung	Wasserversorgung	Wasserversorgung	Wasserversorgung	Wasserversorgung
	498 LocalSubCategory	Bereitstellung	Bereitstellung	Bereitstellung	Bereitstellung	Bereitstellung	Bereitstellung
	499 Formula	H2O	H2O				
	501 StatisticalClassification						
	502 CASNumber						
TimePeriod	601 StartDate	2000	2000	1993	1993	1993	1993
	602 EndDate	2000	2000	1998	1998	1998	1998
	603 DataValidForEntirePeriod	1	1	1	1	1	1
	611 OtherPeriodText	Time of publication.		Time of publication.		Time of publication.	
Geography	663 Text	Infrastructure data for CH. Energy use in DE.		Investigation for CH.		Data provided by a CH company in Marin (NE).	
Technology	692 Text	Example of a water works in CH.		Example of a water works in CH.		Supply network for drinking water.	
Representativeness	722 Percent			10	9	9	9
	724 ProductionVolume	Not known.	Not known.	16040km are in use in CH.	644546 m ³ per year	2500 m ³	1.2 Mio. m ³ per year
	725 SamplingProcedure	Literature.	Literature.	Literature and own estimations	Literature and own estimations	Literature and own estimations	Literature and own estimations
	726 Extrapolations	From CH and DE to RER situation. Share of resource uses (ground and surface water) estimated.		From single data to Swiss situation.		From single data to Swiss situation.	
	727 UncertaintyAdjustments	none	none	none	none	none	none
DataGeneratorAndSource	751 Person	41	41	41	41	41	41
	756 DataPublishedIn	2	2	2	2	2	2
	757 ReferenceToPublishedSource	8	8	8	8	8	8
	758 Copyright	1	1	1	1	1	1
	759 AccessRestrictedTo	0	0	0	0	0	0
	760 CompanyCode						
	761 CountryCode						
	762 PageNumbers	chapter water	chapter water	chapter water	chapter water	chapter water	chapter water

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93 Water, deionised

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93.1 Introduction

All naturally occurring water contains dissolved mineral salts. In solution, salts separate into positively charged cations and negatively charged anions. Deionisation can reduce the amounts of these ions to very low levels through the process of ion exchange. Ion exchangers exist in four basic forms: disposable cartridges, portable exchange tanks, automatic units, and continuous units. Two-bed systems employ separate cation and anion resin beds while mixed-bed deionisers work with both resins in the same vessel. Mixed-bed deionisers produce the highest quality of deionised water, while two-bed deionisers have a larger capacity. For this inventory, automatic units with a two-bed system were considered.

Cations are removed by cation exchange resin. It replaces sodium, calcium, magnesium and other cations with hydrogen ions (H). This exchange produces acids, which must be removed or neutralised by an anion exchange resin. Two types of anion resin are used for deionisation: weak base resin and strong base resin. Weak base resin absorbs strong acids, while strong base resin exchanges chloride, sulphate, and alkaline anions for hydroxide ions (OH). The hydrogen ions from the cation exchange process and hydroxide ions from the anion exchange form water.

For the assessment of deionised water, the quality of the raw water is the most important parameter to calculate the amount of regeneration chemicals and the volume of resin used. It was assumed that the water source for the deionising process would be tap water. For this inventory, the drinking water quality of Zurich and Basel (Hardwasser) was used as a reference (Stadt Zürich 2001, Hardwasser 2000). The concentration of the different ions in the raw water and the average values used for this inventory are shown in the following table.

Tab. 93.1 Chemical properties of drinking water in Zurich and Basel. Average raw water composition used.

Property	Formula	Unit	Hardwasser (Basel), ¹	Average value for Zurich, ²	Average for this inventory
Total hardness	-	mol m ⁻³	1.84	1.58	1.71
French hardness	-	°fH	18.40	15.80	17.05
German hardness	-	°dH	10.30	8.85	9.55
Calcium	Ca ⁺⁺	mol m ⁻³	1.50	1.28	1.39
Magnesium	Ca ⁺⁺	mol m ⁻³	0.33	0.30	0.32
Sodium	Na ⁺	mol m ⁻³	0.42	0.20	0.29
Potassium	K ⁺	mol m ⁻³	0.04	0.03	0.04
Chloride	Cl ⁻	mol m ⁻³	0.32	0.13	0.20
Sulphate	SO ₄ ⁻⁻	mol m ⁻³	1.17	0.41	0.69
Nitrate	NO ₃ ⁻	mol m ⁻³	0.11	0.07	0.09
Phosphate	PO ₄ ³⁻	mol m ⁻³	no data	0.19 * 10 ⁻³	0.19 * 10 ⁻³
Silica, as SiO ₂	SiO ₂	mol m ⁻³	no data	0.06	0.06
Bicarbonate	HCO ₃ ⁻	mol m ⁻³	no data	2.87	2.93 , ³
Free CO ₂	CO ₂	mol m ⁻³	no data	0.10	0.10

¹ Composition of drinking water obtained from "Hardwasser" well in Basel. Values for year 2000 (Hardwasser 2000)

² Composition of drinking water in Zurich. Average values for year 2001 (Stadt Zürich 2001)

³ Value set to obtain ionic balanced water analysis

93.2 Reserves and resources of material

As resource for deionised water, tap water from a public supply was assumed. In large plants deionised water will also be obtained from raw water of river or lakes. In this case further processing steps as filtration or flocculation will be needed. This inventory deals with the production of deionised water in Switzerland. For the applications in Switzerland it was assumed that tap water (or similarly treated plant internal water) would be used in the majority of the cases for the production of deionised water. The average raw water composition listed in Tab. 93.1 was assumed to be representative for the average composition of raw water for industrial processes, because the water sources considered lie within the large industrial areas of Switzerland (Zurich, Basel). The composition of the water resource and therefore the need of treatment chemicals for the deionisation may vary to a large extend. Thus, the total hardness, for example, may be higher than 3 mol m^{-3} (30°fH). This variation is considered in the uncertainty assessment.

93.3 Use of material / product

Deionised (DI) water has become an essential ingredient in many applications including: medical, laboratory, pharmaceutical, cosmetics, electronics manufacturing, food processing, plating and countless other industrial processes. The quality of water needed in the different applications varies considerably. E.g., the conductivity (used as quality parameter) for demineralised water is $1\text{-}10 \mu\text{S cm}^{-1}$. Such water is used as boiler feed water for boilers up to 30 bar pressure. On the other hand, the conductivity of completely demineralised water is in the range of $0.055\text{-}1.0 \mu\text{S cm}^{-1}$. The purest water is used within the wafer and electronic circuit production. For the process analysed in this inventory the production plant includes a strong cation exchanger, a degasser, and a strong anion exchanger. Such systems obtain, by operation with counterflow regeneration, a water conductivity of $1 \mu\text{S cm}^{-1}$ and a silica content (as SiO_2) of $5\text{-}25 \mu\text{g l}^{-1}$ (Ullmann 2002).

93.4 Systems characterization

The production of deionised water in this inventory was assessed considering ion exchange with a strong cation exchanger, a degasser, and a strong anion exchanger. Other possible production methods such as reverse osmosis electrodialysis or distillation were not considered. The following processes were modelled:

- Water, deionised, at plant (location: CH); see Fig. 93.1
- Water treatment plant, deionisation (location: CH); see Fig. 93.2
- Cationic resin, at plant (location: CH); see Fig. 93.3
- Anionic resin, at plant (location: CH); Fig. 93.4

The functional unit for deionised water is 1 kg of deionised water in this inventory. The infrastructure of the ion exchanger plant to produce this deionised water is modelled in the process „water treatment plant, deionisation”.

The processes for anionic and cationic resin include the production for strong cation exchanger resins and strong anion exchanger resins. Concerning these processes, the main raw materials and an approximation of the energy demand is considered. These modules are only to use as a rough estimation of the process requirements. For the inventory of deionised water, the quality of these modules was assumed to be sufficient, because only small amounts of resin are replaced regarding the total water throughput.

The functional unit of the resins is 1 kg of *moist* resin. The moisture content of the assessed resins is 50 wt-% which corresponds to a resin with 6-8 wt-% divinylbenzene (DVB) crosslinking.

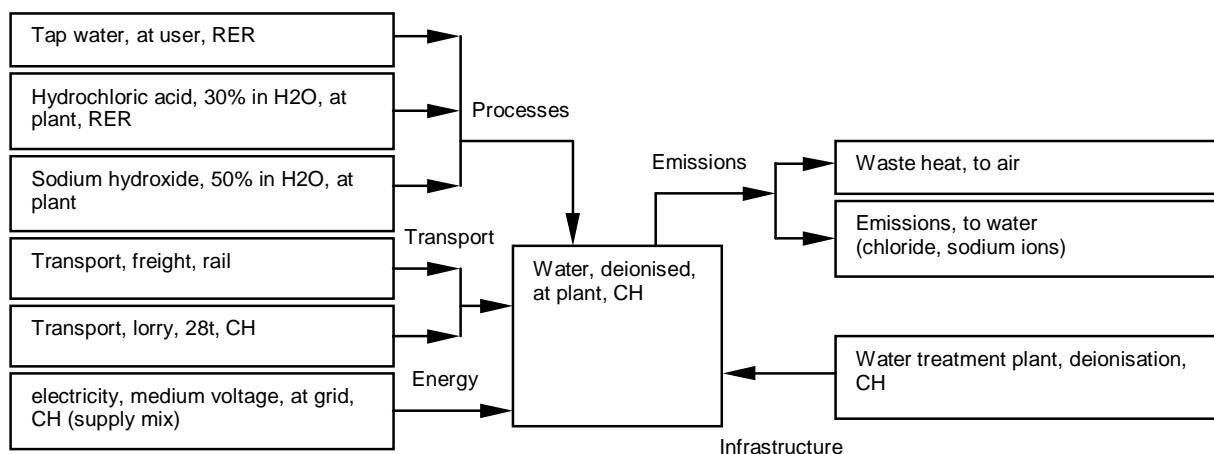


Fig. 93.1 Process chain for the production of deionised water.

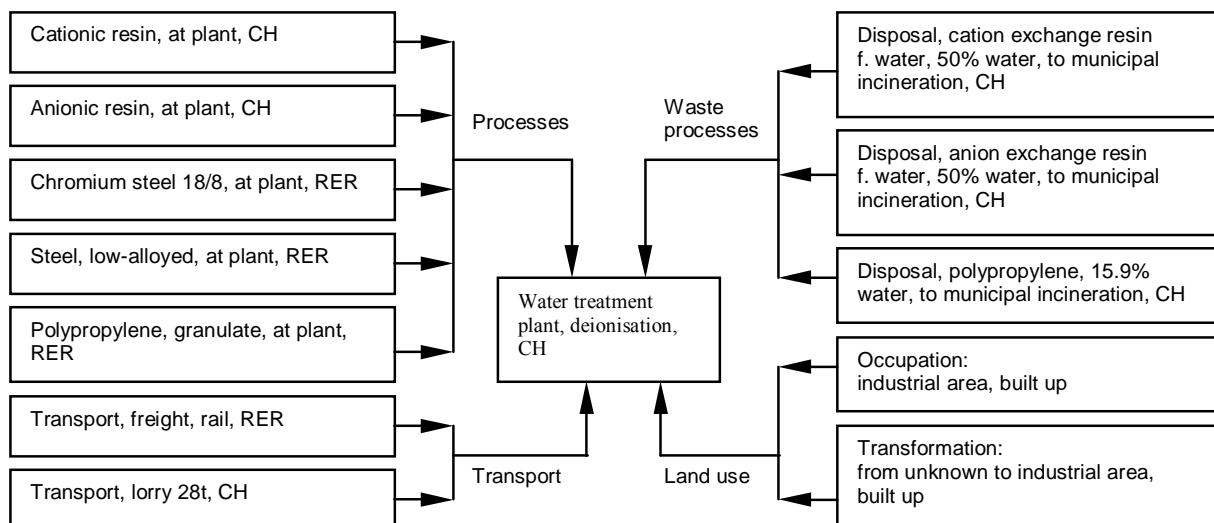


Fig. 93.2 Process chain for the infrastructure of the deionised water production.

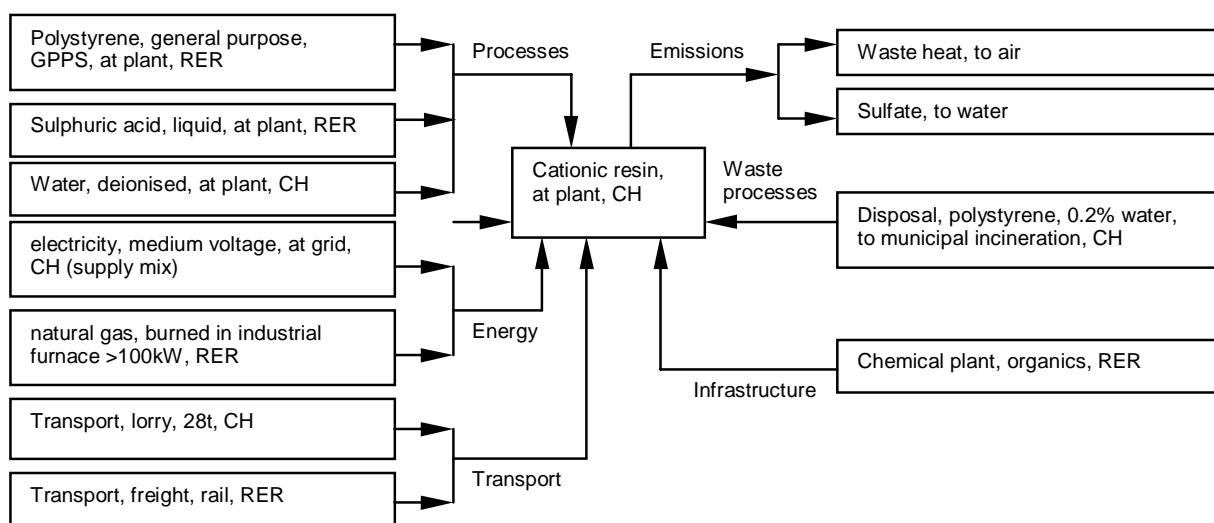


Fig. 93.3 Process chain for the production of strong cationic ion exchange resin.

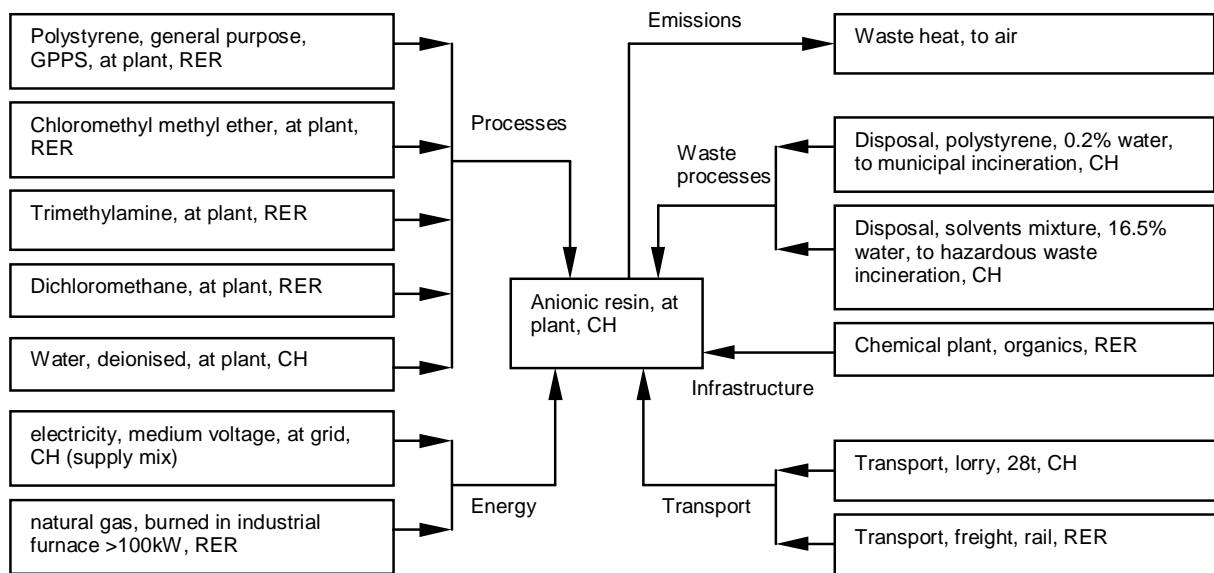


Fig. 93.4 Process chain for the production of strong anionic ion exchange resin.

93.5 Water, deionised, at plant

93.5.1 Process

The process analysed includes a strong cation exchanger, a degasser, and a strong anion exchanger. It was assumed that the unit is operated with counterflow regeneration. The obtained water quality in this process will reach about a value of $1 \mu\text{S cm}^{-1}$ for the conductivity and a silica content (as SiO_2) of $5\text{--}25 \mu\text{g l}^{-1}$ in the produced water. Fig. 93.5 presents a simplified scheme of the assessed production process for deionised water.

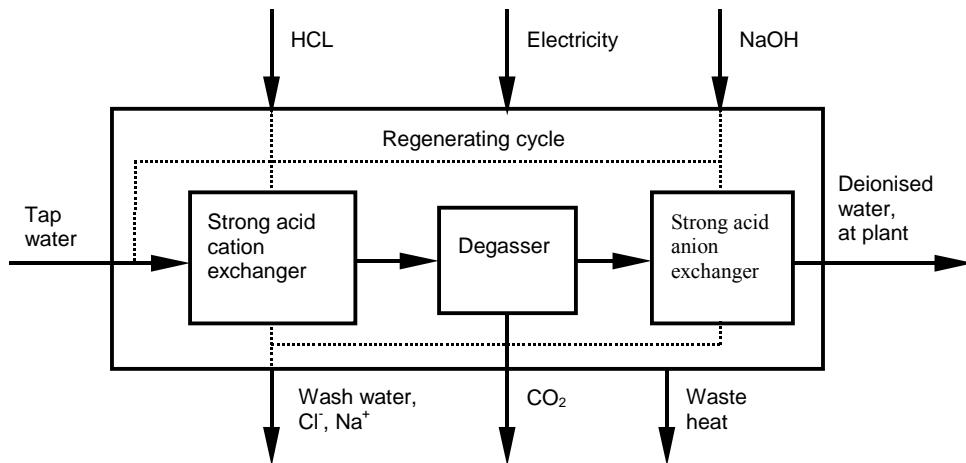


Fig. 93.5 Simplified process of deionisation of water

As regeneration chemicals sodium hydroxide and hydrochloric acid are considered. Further, water for regeneration and electricity for the operation is needed. The salts produced by the regeneration chemicals are considered as water emissions. The disposal of the used ion exchanger resin is not considered within the production process, because the lifetime of the resin is long (about 5 years) and the replacement is not a normal plant operation. The replacement and disposal of the resin is included in the infrastructure module.

93.5.2 Resources

Electricity

Electricity is needed to pump the water through the exchanger beads, for the pumping of water and chemicals within the regeneration step and for the blower in the CO₂-stripping column. The amount reported for the electricity consumption ranges from 0.24 kWh m⁻³ for the operation of a plant producing 30 m³ h⁻¹ of deionised water in the glass industry UNIDO 1992 to 0.82 kWh m⁻³ for the production of deionised water in the chemical industry (Jödicke 2001). According to Mavrov et al. 1999 the energy demand per m³ deionate is 0.3 kWh for a plant with lime decarbonization, filtration and total desalination with ion exchanger (cation exchanger, anion exchanger, mixed bed ion exchanger). A much higher amount of electricity is needed if the production process includes besides ion exchange also reverse osmosis. For deionised water used in clean room processes an electricity demand of 2.51 kWh m⁻³ and for ultra pure water as used in chip manufacturing 12 kWh m⁻³ are reported (Ast et al. 2002). Those values were not considered in this inventory because of the use of other technology (reverse osmosis) and the higher product water quality than the one defined in chapter 93.3. As average electricity demand for this inventory a value of 0.45 kWh m⁻³ (or 0.45 * 10⁻³ kWh kg⁻¹) was used. This value corresponds to the geometric mean between the values reported in UNIDO 1992 and Jödicke 2001. For the electricity demand, the supply mix for Switzerland (medium voltage) was applied. A summary of the values used is given in Tab. 93.2.

Regeneration chemicals

For regeneration, sodium hydroxide and hydrochloric acid is used. The amount of regeneration chemical used is strongly dependent on the hardness of the water and the service requirements. For this inventory the demand was calculated from the assumed water composition (see Tab. 93.1.). For full regeneration, more than the stoichiometric amount of chemicals is needed. According to an example unit calculated in Ullmann 2002, Table 7, for a strong acidic cation exchanger an amount of 210% and for a strong base anion exchanger 306% of the theoretical amount of regeneration chemicals is needed. According to calculations carried out with a calculation and design software (Lewatit 2002) for the given raw water quality (see Tab. 93.1) the following average value and range for the amount of regeneration chemicals needed were calculated:

- Strong acidic cation exchanger: 0.24 kg m⁻³ HCl (100%) or 176% of the theoretical demand; Range between 0.21 – 0.28 kg m⁻³ HCl (100%) or 153% - 202% of the theoretical demand.
- Strong base anion exchanger: 0.12 kg m⁻³ NaOH (100%) or 266% of the theoretical demand; Range between 0.09 – 0.15 kg m⁻³ NaOH (100%) or 205% - 345% of the theoretical demand.

These calculations base on an exchanger design with a strong acidic cation column, a degasser and a strong base anion resin column, which use no lime decarbonisation as pre-treatment (only filtration). The plant was assumed to use counter current regeneration in order to achieve a low product water conductivity (1 µS cm⁻¹) and low silica concentration. The calculations were executed for different resin types. The average values of the calculations were used for this inventory. These values are uncertain due to the possibly different composition of the water, which may increase or decrease the demand of regeneration chemicals. Also the design and operation mode of the plant influences the values largely. These influences are not included in the range of regeneration chemicals stated above.

Dependant on the ionic load of the raw water the consumption of regeneration chemicals can differ by a factor of two (higher or lower) if raw water with a range of hardness (Ca and Mg) between 0.7 and 3.2 mol m⁻³ (7 to 32 °FH) is used. Under these conditions, the differences within the regeneration chemicals consumption given by Jödicke 2001 and UNIDO 1992 can be explained. The total uncertainty for the assessment was calculated from the range of raw water quality (factor 2) and the range due to different resin types (factor 1.18 for HCl, 1.12 for NaOH). This leads to the uncertainty scores of 2.04 for HCl and 2.02 for NaOH presented in **Fehler! Verweisquelle konnte nicht gefunden werden.**

Water use

Water is used for backwash, rinsing and the dilution of the regenerating chemicals. The wash water demand is given as 6% of the produced water for co-current regeneration and 2 times the resin volume for counter current regeneration (Sybron Chemicals 2002). Calculated per m^3 produced water this leads to a water demand of about 1-2% of the production. Other sources give a value of 6-10 m^3 per m^3 resin volume for backwash displacement rinse and fast rinse (ResinTech 2002). Calculated per m^3 produced water, this leads to a water demand of about 2-5% of the production. The treatment chemicals are diluted for the regeneration step to 4-6% for HCl and 2-4% for NaOH (Sybron Chemicals 2002). This leads to an additional water demand of about 1% of the production. According to Mavrov et al. 1999 the total water demand per m^3 deionate is 1.11 m^3 for a plant with lime decarbonisation, filtration, and total desalination with ion exchanger (cation exchanger, anion exchanger, mixed bed ion exchanger). According to calculations executed with a calculation and design software (Lewatit 2002), the total water demand ranges between 1.02 $\text{m}^3 \text{ m}^{-3}$ and 1.22 $\text{m}^3 \text{ m}^{-3}$ for the given raw water quality (see **Fehler! Verweisquelle konnte nicht gefunden werden.**). For this inventory, a total water use (including the product water) of 1.11 $\text{m}^3 \text{ m}^{-3}$ (or 111%) was applied. As limits for the total water consumption in the production of deionised water for industrial processes, a range from 102% to 122% of the production was assumed.

For applications in clean room technologies, a total water demand of 140% of the production and for ultra pure water used in chip manufacturing, a demand of 300% of the production is reported (Ast et al. 2002). Those values were not considered in this inventory because of the use of a different technology (reverse osmosis), which has a higher water demand and achieves a higher water quality than the one defined in chapter 93.3.

Transport

The transport needed for the treatment chemicals were considered with the standard distances of 600 km rail transport and 50 km road transport. For the transport of 0.24 kg m^{-3} HCl (100%) and 0.12 kg m^{-3} NaOH (100%), also the weight of the water contained in the 30% HCl solution and the 50% NaOH solution was considered. This leads to a total weight concerned for the transport of $1.04 * 10^{-3}$ kg treatment chemicals per kg deionised water. With the assumed transport distances, this leads to $624 * 10^{-6}$ tkm rail transport and $52 * 10^{-6}$ tkm lorry transport (28 t) per kg deionised water.

93.5.3 Emissions

Waste heat and emissions to air

It was assumed, that 100% of the electricity consumed (1.62 MJ m^{-3}) is converted to waste heat and, as such, released to the air.

A small amount of CO₂ is released from the degassing unit due to the release of carbonic acid in the water. Of the initial 2.93 mol HCO₃ per m^3 water (Tab 1.1) approximately 0.2 mol remain in the water after degassing. Therefore, approximately 2.73 mol HCO₃ are converted to CO₂. This corresponds to an emission of $2.3 * 10^{-4}$ kg CO₂/kg water. Further emissions to air were not considered.

Waste water

The rinse and backwash water will be emitted from the plant. The wastewater contains chemicals used for regeneration. The amount of regeneration chemicals used in this inventory leads to an emission of 0.23 kg m^{-3} Cl⁻ and 0.07 kg m^{-3} Na⁺. Further emissions to the water as the ions removed from the raw water, which are released, again during the regeneration step, were not considered.

Solid wastes

The only solid waste generated is the spent ion exchanger. This waste was not considered as normal production waste and is therefore reported within the infrastructure module.

Tab. 93.2 Energy demand, resource demand and emissions for the production of deionised water.

Resource, emission	Unit	per kg deionised water	Range; per kg deionised water
Electricity, medium voltage, at grid, CH	kWh	$0.45 * 10^{-3}$; ¹	$0.24 * 10^{-3} - 0.82 * 10^{-3}$
Tap water, at user	kg	1.11; ¹	1.02 – 1.22
Hydrochloric acid, 30% in H ₂ O, at plant ; ²	kg	$0.24 * 10^{-3}$	$0.20 * 10^{-3} - 0.28 * 10^{-3}$
Sodium hydroxide, 50% in H ₂ O, at plant ; ²	kg	$0.12 * 10^{-3}$	$0.09 * 10^{-3} - 0.15 * 10^{-3}$
Transport, freight, rail	tkm	$624 * 10^{-6}$	not determined
Transport, lorry 28t	tkm	$52 * 10^{-6}$	not determined
Waste heat to air	MJ	$1.62 * 10^{-3}$	0.86 – 2.95
Chloride, Cl- ; ²	kg	$0.23 * 10^{-3}$	$0.19 * 10^{-3} - 0.27 * 10^{-3}$
Sodium, Na+ ; ²	kg	$0.07 * 10^{-3}$	$0.05 * 10^{-3} - 0.09 * 10^{-3}$
Water treatment plant, deionisation	unit	$90 * 10^{-12}$	not determined

¹ Value calculated as geometric average of the values reported as range.

² Value depends largely on the water composition; Range does not include variations in the water quality and refers only to plants with a strong acidic cation exchanger followed by a degasser and a strong base anion exchanger, which are operated with counter current regeneration. The range of raw water quality is considered in the uncertainty (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

93.5.4 Infrastructure

The infrastructure of the deionisation unit refers to a production of 100 m³ deionised water per hour and a plant lifetime of 15 years. It was assumed that the plant availability is 85% or 7500 h per year. Therefore, the infrastructure has to be divided by a production of $11 * 10^6$ m³ deionised water in the whole lifetime. With this product output an infrastructure value of $90 * 10^{-9}$ units per m³ of deionised water were calculated.

93.6 Water treatment plant, deionisation

The main components of the water deionisation plant are the resin beads. The granular resin is filled in tanks of acid resistant or lined steel. The tank volume is about 1.6 times the volume of the resin (60% space for backwash operation). Further parts of the equipment are the degasser, which frees the water from carbonic acid, and various pumps pipes and storage tanks for the treatment chemicals.

The plant assessed in this inventory uses a cation resin volume of 5.3 m³ and an anion resin volume of 2.8 m³ according to the design calculations carried out for the given raw water quality (see beginning of this chapter). The lifetime of the unit is 15 years and it was assumed that the resin is replaced every 4 to 6 years Gottlieb 1997. The unit produces 100 m³ deionised water per hour with a running time of 12 hours. Because of the regenerating process (ca. 2 h) the production time is only 85% of the operating time. This leads to a production of about $11 * 10^6$ m³ deionised water within the lifetime of the unit.

The resin has to be exchanged 2 times within the lifetime and in addition the initial resin production has to be included. The densities of the moist resin given in Ullmann 2002 were used for this inventory. For the strong acidic cation resin 1.28 kg l⁻¹ and for the strong base anion resin 1.10 kg l⁻¹ were

used. This leads to a total amount of 15.9 m³ (20.35 t) strong acidic cation resin and 8.4 m³ (9.24 t) strong base anion resin.

Further steel and plastic parts are used for the tanks, pipes and other parts. From data of a decarbonising unit, the total weight of the equipment (with resin) was estimated to be about the double of the resin weight alone (Christ 2002). With this assumption an equipment weight of about 9.9 t was estimated. From this weight it was assumed that 60% or 5.9 t is stainless steel, 30% or 3 t is low-alloyed steel and 10% or 1 t is polypropylene (liner).

For the transportation of the materials the standard distances were applied for steel (600 km rail, 50 km road) and plastic (200 km rail, 50 km road). For the resin the same distances as for plastic was used. For the transportation of the polypropylene parts and the moist resin to the disposal site (incineration), 10 km road transport were assumed. For the polypropylene parts an additional weight of 15.9% water in the waste have to be considered, which leads to a total transport weight of 0.83 t. For the resin the same weight (50% water content) as for the new resin was assumed (same moisture content). This leads to a total amount for transportation of 11500 tkm rail transport and 2280 tkm road transport (lorry 28 t).

For the disposal of the plant it was assumed that the metals will be recycled and therefore no burden was accounted. For the polypropylene used it was assumed that it would be burned in a municipal incineration plant. Also the 20 t of moist resin used during the lifetime of the plant will be burned in a municipal incineration plant. For the incineration the composition of the exhausted resin and the high water content (50%) was considered.

The elemental composition of the used resins was calculated from the composition and the ion loading according to the distribution in the raw water considered (see **Fehler! Verweisquelle konnte nicht gefunden werden.**). The composition of the resin itself was calculated as styrene with 8 wt.-% cross-linked di-vinyl benzene. For the strong anion exchanger resin quaternary amine was considered as functional group and for the strong cation resin a sulphonic acid group. The calculated elemental composition is presented in the following table.

Tab. 93.3 Calculated elemental composition of strong anion resin and strong cation resin sent to the incineration

Resin type	Unit	Element concentration (wet weight)								
		H ₂ O	C	H	S	O	Ca	Mg	Na	K
Strong cation resin ¹	wt-%	50.00	25.46	1.91	7.36	11.02	3.344	0.265	0.538	0.094
		H ₂ O	C	H	S	O	N	Cl	P	Si
Strong anion resin ²	wt-%	50.00	32.71	4.02	2.40	7.03	2.86	0.79	0.001	0.19

¹ Styrene bead cross-linked with 8 wt.-% DVB. Sulphonic acid as functional group. Loaded with Ca, Mg, Na, K

² Styrene bead cross-linked with 8 wt.-% DVB. Quarternary amine as functional group. Average composition between 50% type I and 50% type II resin. Loaded with N, Cl, P, Si

The area occupied by the plant was estimated to be 100 m², extrapolated from the space requirements for a 30 m³ h⁻¹ plant given in UNIDO 1992. With the assumed lifetime, the occupation is 1500 m² a. The occupation was accounted as “industrial area built up”. The land use before plant erection is not known. There was no occupation as construction site included because the plants are erected within very short time and this occupation was therefore neglected. **Fehler! Verweisquelle konnte nicht gefunden werden.** shows a summary of the values used for the infrastructure process of the production of deionised water.

Tab. 93.4 Land use and used processes for a water treatment plant for deionisation

Resource, Disposal process, Land use	Unit	per unit (plant)	per kg deionised water
Cationic resin, at plant	kg	2.04E+04	1.83E-06
Anionic resin, at plant	kg	9.24E+03	8.32E-07
Chromium steel 18/8, at plant	kg	5.90E+03	5.31E-07
Steel, low-alloyed, at plant	kg	3.00E+03	2.70E-07
Polypropylene, granulate, at plant	kg	1.00E+03	9.00E-08
Disposal, cation exchange resin f. water, 50% water, to municipal incineration	kg	2.04E+04	1.83E-06
Disposal, anion exchange resin f. water, 50% water, to municipal incineration	kg	9.24E+03	8.32E-07
Disposal, polypropylene, 15.9% water, to municipal incineration	kg	1.19E+03	1.07E-07
Transport, freight, rail, RER	t km	1.15E+04	1.03E-06
Transport, lorry 28t, CH	t km	2.28E+03	2.05E-07
Occupation, industrial area, built up	m ²	1.50E+03	1.35E-07
Transformation, to industrial area, built up, ¹	m ² a	1.00E+02	9.00E-09

¹ Transformation from unknown to industrial area, built up

93.7 Cationic resin, at plant

93.7.1 Process

This process includes a rough estimation of the production process of a strong acidic cation exchanger resin for water treatment. Due to missing production data this inventory bases on stoichiometric calculations. For these calculations a process yield of 95% for the used chemicals and the copolymer was assumed. The process energy demand was approximated with data from a large chemical plant site (Gendorf 2000). Due to these approximations the uncertainty within the results of this inventory is large.

For this inventory the functional unit is 1 kg of moist (hydrated) cation exchanger resin. The most important physical properties used in this inventory are given in Tab. 93.5.

Tab. 93.5 Chemical and physical properties of a strong acidic cation exchanger resin

Property	Unit	Value	Remarks
Bulk weight, moist (hydrated)	1.28	kg m ⁻³	as supplied to customer
Moisture content	50	wt.-%	equals about 6-8% DVB cross linking
Total capacity	1.7 – 2.0	eq l ⁻¹	dependent on ionic form of resin
Operating capacity	0.7 – 1.2	eq l ⁻¹	dependent on ionic form and operation

The manufacturing process for cation exchanger resins is described in Keller 1997 and consists of the polymerisation of the styrene and divinylbenzene, the sulfonation with sulphuric acid and a rinsing process.

In the polymerisation process styrene and divinylbenzene (DVB) as cross-linking agent are mixed in a suspension system. This process leads to hardened spherical plastic beads. Standard resins used for water treatment processes are 8 wt-% DVB cross-linked. In this inventory the production of this cross-

linked copolymer beads was approximated with linear polystyrene. Due to the comparable chemical production process of styrene and divinylbenzene this simplification was assumed to have no major influence on the result.

The copolymer is then dried and screened to meet the resin specifications. The next production step is the sulfonation of the copolymer to produce the functional groups needed for ion exchange. In this step the copolymer is treated with concentrated sulphuric acid or chlorosulfonic acid under elevated temperatures (about 80 °C). The last step consists in rinsing the functionalized copolymer. This is performed by hot water washing and steaming the resin to reduce the amount of organic compounds left in the resin from the manufacturing process. At this point, the cation resin is in the hydrogen form which is the form desired for this inventory. If the resin is needed in a sodium form (Na^+) it has to be neutralised with NaOH. This neutralisation step is not included in this inventory. Fig. 93.6 gives a simplified scheme of the assessed production process for the strong acidic cation exchanger resin.

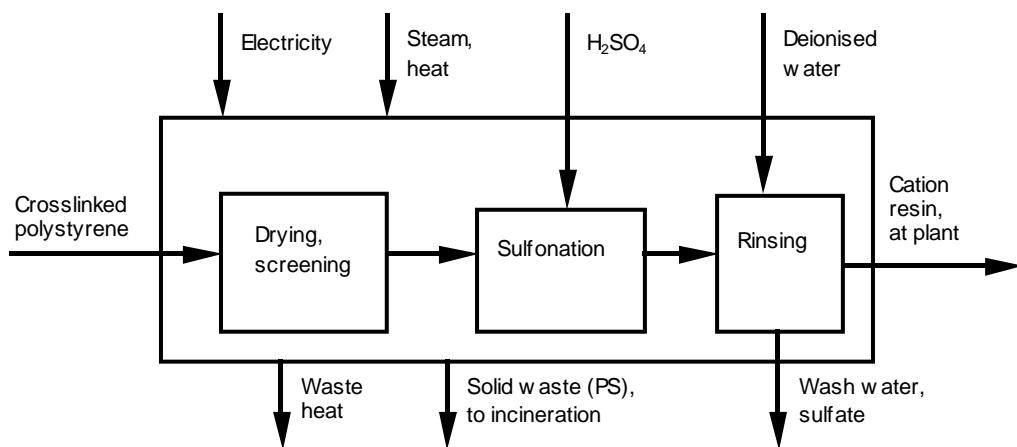


Fig. 93.6 Simplified process for the production of strong acidic cation exchanger resin

93.7.2 Resources

Energy

Electricity is needed to run the mixing of the suspension and the pumps. Fossil fuel is needed to generate the desired heat for the production process, the drying and the steam for the rinsing process. There was no information available on the amount of energy used for those processes. The process energy demand was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf 2000). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the cation resin production process. This total energy demand was covered with natural gas (50%), electricity (38%), and steam from external energy sources (12%). For this inventory all energy used for heat or steam was assumed to be natural gas. An amount of 2 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was assumed. A summary of the values used is given in Tab. 93.6.

Raw materials and chemicals

For the production of 1 kg activated cation exchanger resin (hydrated) the following stoichiometric inputs are needed (yield 100%):

- Styrene, C₈H₈: 0.269 kg (2.59 mol)

- Divinylbenzene, C₁₀H₁₀: 0.023 kg (0.18 mol)
- Sulphuric acid, H₂SO₄: 0.254 kg (2.59 mol)
- Deionised Water, H₂O: 0.5 kg (27.75 mol)

In this inventory the production of the 8 wt-% DVB cross-linked styrene beads was approximated with linear polystyrene. For the production a yield of 95% was assumed. To produce 1 kg activated cation exchanger resin with a moisture (H₂O) content of 50 wt.-%, 0.308 kg polystyrene and 0.267 kg sulphuric acid were therefore considered as raw materials and process chemicals in this inventory. A summary of the values used is given in Tab. 93.6.

Water use

To hydrate the activated cation exchanger resin 50 wt-% or 0.5 kg deionised water is need. Further, an amount of 5 bed volumes was estimated to be needed to rinse the produced resin. Using a density of 1.28 kg l⁻¹ for the moist resin (Ullmann 2002), the demand of rinse water is 3.9 kg. In total a demand of 4.4 kg deionised water was considered.

Transport

For the transportation of the materials the standard distances were applied for sulphuric acid (600 km rail, 50 km road) and for polystyrene (200 km rail, 50 km road). For the transportation of the solid polystyrene waste to the disposal site (incineration), 10 km road transport were assumed. This leads to a total amount of 0.222 tkm rail transport and 0.029 tkm road transport (lorry 28 t) per kg produced resin.

93.7.3 Emissions

Waste heat and emissions to air

It was assumed that 100% of the electricity consumed or 1.2 MJ per kg resin is converted to waste heat and, as such, released to the air. Further emissions to air were not considered.

Waste water

The used rinse water will be emitted from the plant. As emissions to water only the amount of sulphuric acid used above the stoichiometric amount was considered (accounted as sulphate). Therefore, 0.013 kg sulphate (SO₄⁻) per kg resin was considered as emission to water. Further emissions to water were not considered.

Solid wastes

It was assumed that 5% of the polymer input, or 0.015 kg per kg moist product resin is lost during the production because it does not meet the specifications (rejected during the screening before the activation step). This solid (dry) polystyrene waste was assumed to be incinerated. For this waste the process “disposal, polystyrene, 0.2% water, to municipal incineration” was used. No further solid wastes were considered.

Infrastructure and land use

No information was available about the infrastructure need of the production plant. It was assumed that the importance of infrastructure is low and therefore the module “chemical plant, organics” was

used as approximation. For this module with a production capacity of 50'000 t per year and a plant lifetime of 50 years, an amount of $4 * 10^{-10}$ units per kg moist product resin was included.

Tab. 93.6 Energy demand, resource demand, and emissions for the cation exchanger resin production.

Resources, emissions	Unit	Value per kg Resin	Remarks
Polystyrene, general purpose, GPPS, at plant; ¹	kg	0.308	Approximation for DVB cross linked polystyrene, 95% yield
Sulphuric acid, liquid, at plant	kg	0.267	For sulfonation, 95% yield
Electricity, medium voltage, at grid; ²	kWh	0.333	Estimation
Natural gas, burned in industrial furnace >100kW; ²	MJ	2	Estimation
Water, deionised, at plant	kg	4.4	Moisture of resin and for rinsing
Waste heat, to air	MJ	1.2	From electricity demand
Sulphate, to water	kg	0.013	5% of the sulphuric acid input
Disposal, polystyrene, 0.2% water, to municipal incineration	kg	0.015	5% of the polystyrene input
Transport, lorry, 28t	tkm	0.029	Calculated with standard distances
Transport, freight, rail	tkm	0.222	Calculated with standard distances
Chemical plant, organics	unit	$4 * 10^{-10}$	Approximation for infrastructure

¹ Production of the 8 wt-% DVB cross-linked styrene beads was approximated with linear polystyrene

² Approximated with data from a large chemical plant site in Germany (Gendorf 2000).

93.8 Anionic resin, at plant

93.8.1 Process

This process includes a rough estimation of the production process of a strong base anion exchanger resin for water treatment. Due to missing production data this inventory bases on stoichiometric calculations. For these calculations, a process yield of 95% for the used chemicals and the copolymer was assumed. The process energy demand was approximated with data from a large chemical plant site (Gendorf 2000). Due to these approximations the uncertainty within the results of this inventory is large.

There are two types of strong base anion resins. The type I uses trimethylamine (TMA) to functionalise the resin, while type II is functionalised with dimethylethanolamine (DMEA). Type I anion resins have a higher stability of the exchange site and greater affinity to weak bases like silica and alkalinity. On the other hand type II anion resins have a greater operating capacity than type I.

In this inventory the production of a type I strong base anion exchanger resin was assessed. The functional unit is 1 kg of moist (hydrated) anion exchanger resin. The most important physical properties used in this inventory are given in Tab. 93.7.

Tab. 93.7 Chemical and physical properties of a strong base anion exchanger resin

Property	Unit	Value	Remarks
Bulk weight, moist (hydrated)	kg m^{-3}	1.10	as supplied to customer
Moisture content	wt.-%	50	equals about 6-8% DVB cross linking
Total capacity	eq l^{-1}	1.1 – 1.5	dependent on ionic form of resin
Operating capacity	eq l^{-1}	0.4 – 0.7	dependent on ionic form and operation

The manufacturing process for anion exchanger resins is described in Ullmann 2002 and consists of the polymerisation of styrene and divinylbenzene, the chloromethylation with chloromethyl methyl ether followed by amination and a rinsing process to clean the produced resin.

In the polymerisation process styrene and divinylbenzene (DVB) as cross-linking agent are mixed in a suspension system. This process leads to hardened spherical plastic beads. For this inventory a resin cross-linked with 8 wt-% DVB was assumed. The production of this cross-linked copolymer beads was approximated with linear polystyrene. Due to the comparable chemical production process of styrene and divinylbenzene, this simplification was assumed to have no major influence on the result.

The copolymer is then dried and screened to meet the resin specifications. The next production step is the chloromethylation and amination of the copolymer to produce the functional groups needed for ion exchange. In a first step the cross-linked polymer is functionalised via Friedel-Crafts chloromethylation reaction using chloromethyl methyl ether (CMME) at 50°C in presence of anhydrous ZnCl_2 or aluminium chloride as catalyst. In this inventory the catalysts were neglected. From this reaction a stoichiometric amount of methanol occurs as waste. In addition a solvent is used within this production step, which leads to further liquid wastes (not regenerated part of the solvent input).

In a second step the chloromethylated group is replaced by an amine. The strong base anion resin investigated (type I) is treated with trimethylamine to obtain a quaternary ammonium group. The last step consists of rinsing the functionalised copolymer. This is performed by hot water washing and steaming the resin to reduce the amount of organic compounds left in the resin from the manufacturing process. At this point, the cation resin is in the chlorine form. If the resin is needed in a free base form (OH^-) it has to be regenerated with NaOH . This regeneration step is not included in this inventory. Fig. 93.7 gives a simplified scheme of the assessed production process for the strong base anion exchanger resin.

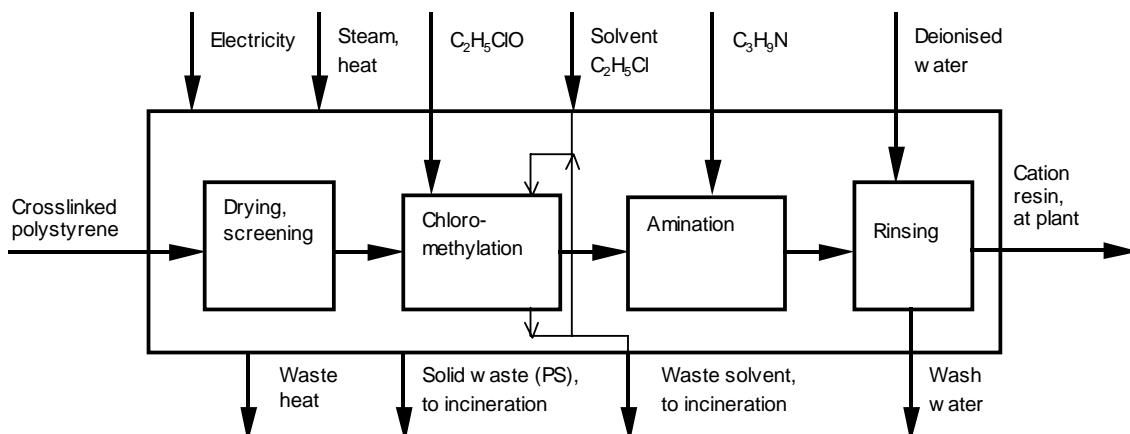


Fig. 93.7 Simplified process for the production of strong base anion exchanger resin

93.8.2 Resources

Energy

Electricity is needed to run the mixing of the suspension and the pumps. Fossil fuel is needed to generate the desired heat for the production process, the drying and the steam for the rinsing process. There was no information available on the amount of energy used for those processes. The process energy demand was approximated with data from a large chemical plant site in Germany producing 2.05 Mt a⁻¹ (intermediates included) of different chemicals (Gendorf 2000). The values for the energy consumption per kg of product of this plant (3.2 MJ kg⁻¹) were used as approximation for the energy consumption of the anion resin production process. This total energy demand was covered with natural gas (50%), electricity (38%), and steam from external energy sources (12%). For this inventory all energy used for heat or steam was assumed to be natural gas. The solvent distillation was considered as separate production step, which requires additional energy. According to Hofstetter 2002 about 1 kg steam per kg recovered solvent is needed for the distillation of a solvent with low heat of evaporation (such as toluene or dichloromethane). For this inventory a natural gas demand of 3.2 MJ per kg recovered solvent was used. This leads to an additional gas demand of 4.3 MJ per kg of product resin to regenerate 1.33 kg waste solvent (85%). For this inventory in total an amount of 6.3 MJ kg⁻¹ natural gas and 1.2 MJ kg⁻¹ electricity was used. A summary of the values used is given in Tab. 93.8.

Raw materials and chemicals

For the production of 1 kg activated anion exchanger resin (hydrated) the following stoichiometric inputs are needed (yield 100%):

- Styrene, C₈H₈: 0.236 kg (2.26 mol)
- Divinylbenzene, C₁₀H₁₀: 0.021 kg (0.16 mol)
- Chloromethyl methyl ether, C₂H₅ClO: 0.182 kg (2.26 mol)
- Trimethylamine, C₃H₉N: 0.134 kg (2.26 mol)
- Deionised water, H₂O: 0.5 kg (27.75 mol)

In this inventory the production of the 8 wt-% DVB cross-linked styrene beads was approximated with linear polystyrene. For the production a yield of 95% was assumed. To produce 1 kg activated cation exchanger resin with a moisture (H₂O) content of 50 wt.-% therefore 0.27 kg polystyrene, 0.192 kg chloromethyl methyl ether and 0.141 kg trimethylamine were considered as raw materials and process chemicals in this inventory. In addition, a solvent is used to carry out the chloromethylation. According to the description in Weinshenker et al. 2002 trichloromethane may be used for this purpose. An amount of 5.5 mol trichloromethane per mol chloromethyl methyl ether was given in this laboratory scale process. Thereof a total solvent use of 1.57 kg trichloromethane per kg resin was calculated. It was assumed that there is a solvent regeneration (distillation) with a product yield of 85% (Hofstetter 2002). Therefore, only an amount of 0.235 kg trichloromethane per kg produced resin is needed as product input. A summary of the values used is given in Tab. 93.8.

Water use

To hydrate the activated anion exchanger resin, 50 wt-% or 0.5 kg deionised water is need. Further, an amount of 5 bed volumes was estimated to be needed to rinse the produced resin. Using a density of 1.10 kg l⁻¹ for the moist resin (Ullmann 2002), this leads to a rinse water demand of 4.5 kg. In total a demand of 5.0 kg deionised water was considered.

Transport

For the transportation of the materials, the standard distances were applied for the organic chemicals (600 km rail, 50 km road) and for polystyrene (200 km rail, 50 km road). For the transportation of the solid polystyrene waste and the solvent waste to the disposal site (incineration), 10 km road transport were assumed. This leads to a total amount of 0.395 tkm rail transport and 0.046 tkm road transport (lorry 28 t) per kg produced resin.

93.8.3 Emissions

Waste heat and emissions to air

It was assumed, that 100% of the electricity consumed or 1.2 MJ per kg resin is converted to waste heat and, as such, released to the air. Further emissions to air were not considered.

Waste water

The used rinse water will be emitted from the plant. There was no information available on the pollution of this rinse water. There will be some organic pollution from the used treatment chemicals, but this contamination was neglected in this inventory.

Wastes

It was assumed that 5% of the polymer input or 0.013 kg per kg moist product resin is lost during the production because it does not meet the specifications (rejected during the screening before the activation step). This solid (dry) polystyrene waste was assumed to be incinerated. For this waste the process “disposal, polystyrene, 0.2% water, to municipal incineration“ was used.

From the total amount of solvent used, 85% or 1.33 kg will be regenerated with distillation. The rest (0.235 kg dichloromethane) is released as waste solvent. Besides the spent solvent also the over stoichiometric amount of treatment chemicals (0.010 kg chloromethyl methyl ether, 0.007 kg trimethylamine) and the stoichiometric waste occurring during the chloromethylation (0.073 kg methanol) are treated as solvent waste. It was assumed that the waste solvent would be incinerated. For this waste the process “disposal, solvents mixture, 16.5% water, to hazardous waste incineration” was used. The process generates in total 0.324 kg waste solvent. Taking the 16.5% water into account, a total amount of 0.388 kg waste solvent mixture has to be considered for the waste process.

Infrastructure and Land use

No information was available on the infrastructure needs of the production plant. It was assumed that the importance of the infrastructure is low and therefore the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant lifetime of 50 years, an amount of $4 * 10^{-10}$ units per kg moist product resin was included.

Tab. 93.8 Energy demand, resource demand, and emissions for the anion exchanger resin production.

Resources, emissions	Unit	Value per kg Resin	Remarks
Polystyrene, general purpose, GPPS, at plant; ¹	kg	0.270	Approximation for DVB cross linked polystyrene, 95% yield
Chloromethyl methyl ether, at plant	kg	0.192	For chloromethylation, 95% yield
Trimethylamine, at plant	kg	0.141	For amination, 95% yield
Dichloromethane, at plant	kg	0.235	Solvent for chloromethylation; ³
Electricity, medium voltage, at grid; ²	kWh	0.333	Estimation
Natural gas, burned in industrial furnace >100kW; ²	MJ	6.3	Estimation
Water, deionised, at plant	kg	5.0	Moisture of resin and for rinsing
Waste heat, to air	MJ	1.2	From electricity demand
Disposal, polystyrene, 0.2% water, to municipal incineration	kg	0.013	5% of the polystyrene input
Disposal, solvents mixture, 16.5% water, to hazardous waste incineration	kg	0.388	All liquid, organic wastes; consist to 60% of the waste solvent; ³
Transport, lorry, 28t	tkm	0.046	Calculated with standard distances
Transport, freight, rail	tkm	0.395	Calculated with standard distances
Chemical plant, organics	unit	$4 * 10^{-10}$	Approximation for infrastructure

¹ Production of the 8 wt-% DVB cross-linked styrene beads was approximated with linear polystyrene

² Approximated with data from a large chemical plant site in Germany (Gendorf 2000). Additional 4.2 MJ natural gas needed for solvent regeneration.

³ Solvent regeneration with a product yield of 85% assumed.

93.9 Data quality considerations

Tab. 93.9 shows the data quality indicators for the inventory of the deionised water production from tap water in Switzerland. Tab. 93.10 shows the data quality indicators for the infrastructure of the deionised water production (production plant). Tab. 93.11 shows the data quality indicators for the inventory of strong acidic cation resin production. Tab. 93.12 shows the data quality indicators for the inventory of strong base anion resin production. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation, and sample size.

The most important data for the production of deionised water is the demand of regeneration chemicals and electricity. These data were derived from different sources and from calculations and shows a large range depending on raw water quality, plant operation and resin type. The used electricity mix refers to a plant in Switzerland. Therefore, for other locations large differences may occur when using local supply mixes.

In general the infrastructure data for the production of deionised water has a high uncertainty. Because of missing specific data approximations with data from similar processes and estimations were used in this inventory. This concerns especially the materials used for the construction of the plant. The amount of resin used and the lifetime of the resin depend on the raw water quality and refer therefore on the water composition used in this inventory.

The data in the inventory of the anion and cation resin has a high uncertainty, because only few data of the production processes were available. Therefore, the data for the used materials was assessed with stoichiometric calculations and the energy demand was estimated by using an average chemical process as approximation. Further, uncertainty occurs from possibly missing auxiliary materials and further

emissions or wastes. The data sets were assessed as a part of the infrastructure of the deionised water production and therefore the high uncertainty within the data was accepted. Due to this reason these data should not be used for processes where the anion and cation resins play an important role.

Tab. 93.9 In- / outputs for the module “water, deionised, at plant”, location CH

Process output: 1 kg, water, deionised, at plant, CH							
	Name, Location	Value	Unit	Uncertainty			Comment
				Type	Score	St.Dev.	
From technosphere	tap water, at user, RER	1.11E+0	kg	lognorm	nA,nA,nA,nA,nA,nA	1.09	CV calculated from range of the reported values
	hydrochloric acid, 30% in H ₂ O, at plant, RER	2.40E-4	kg	lognorm	nA,nA,nA,nA,nA,nA	2.04	CV calculated from range of resin and raw water
	sodium hydroxide, 50% in H ₂ O, production mix, at plant, RER	1.20E-4	kg	lognorm	nA,nA,nA,nA,nA,nA	2.02	CV calculated from range of resin and raw water
	electricity, medium voltage, at grid, CH	4.50E-1	kWh	lognorm	nA,nA,nA,nA,nA,nA	1.85	CV calculated from range of the reported values
	water treatment plant, deionisation, CH	9.00E-11	unit	lognorm	4.5,1,2,3,5	3.18	Estimated with weak data on plant operation
	transport, freight, rail, RER	6.24E-4	tkm	lognorm	4.5,nA,nA,nA,nA	2.09	Estimated with standard distances
	transport, lorry 28t, CH	5.20E-5	tkm	lognorm	4.5,nA,nA,nA,nA	2.09	Estimated with standard distances
	Heat, waste, to air, high population density	1.62E-3	MJ	lognorm	nA,nA,nA,nA,nA,nA	1.85	Calculated from electricity demand
	Carbon dioxide, biogenic, to air, high population density	1.20E-4	kg	lognorm	nA,nA,nA,nA,nA,nA	2.00	CV calculated from range of raw water quality
	Chloride, to water, river	2.30E-4	kg	lognorm	nA,nA,nA,nA,nA,nA	2.04	Calculated from data of chemical demand
	Sodium, ion, to water, river	7.00E-5	kg	lognorm	nA,nA,nA,nA,nA,nA	2.02	Calculated from data of chemical demand
(1) Emissions							

Tab. 93.10 In- / outputs for the allocated products “water treatment plant, deionisation”, location CH

Process output: 1 unit, water treatment plant, deionisation, CH							
	Name, Location	Value	Unit	Uncertainty			Comment
				Type	Score	St.Dev.	
From technosphere	cationic resin, at plant, CH	2.04E+4	kg	lognorm	4.5,1,2,1,4	1.32	Data from calculations with a design software
	anionic resin, at plant, CH	9.24E+3	kg	lognorm	4.5,1,2,1,4	1.32	Data from calculations with a design software
	polypropylene, granulate, at plant, RER	1.00E+3	kg	lognorm	5.5,1,2,4,5	1.88	Estimated with data from a decarbonisation unit
	chromium steel 18/8, at plant, RER	5.90E+3	kg	lognorm	5.5,1,2,4,5	1.88	Estimated with data from a decarbonisation unit
	steel, low-alloyed, at plant, RER	3.00E+3	kg	lognorm	5.5,1,2,4,5	1.88	Estimated with data from a decarbonisation unit
	disposal, cation exchange resin f. water, 50% water, to municipal incineration, CH	2.04E+4	kg	lognorm	4.5,1,2,1,4	1.32	Data from calculations with a design software
	disposal, anion exchange resin f. water, 50% water, to municipal incineration, CH	9.24E+3	kg	lognorm	4.5,1,2,1,4	1.32	Data from calculations with a design software
	disposal, polypropylene, 15.9% water, to municipal incineration, CH	1.19E+3	kg	lognorm	5.5,1,2,4,5	1.88	Estimated with data from a decarbonisation unit
	transport, freight, rail, RER	1.15E+4	tkm	lognorm	4.5,nA,nA,nA,nA	2.09	Estimated with standard distances
	transport, lorry 28t, CH	2.28E+3	tkm	lognorm	4.5,nA,nA,nA,nA	2.09	Estimated with standard distances
(1)	Occupation, industrial area	1.50E+3	m2a	lognorm	3.4,3,5,3,5	1.68	Data from one plant out of literature
	Transformation, from unknown	1.00E+2	m2	lognorm	3.4,3,5,3,5	2.15	Data from one plant out of literature
	Transformation, to industrial area	1.00E+2	m2	lognorm	3.4,3,5,3,5	2.15	Data from one plant out of literature
(1) Ressources							

Tab. 93.11 In- / outputs for the module “cationic resin, at plant”, location CH

Process output: 1 kg, cationic resin, at plant, CH							
	Name, Location	Value	Unit	Uncertainty			Comment
				Type	Score	St.Dev.	
From technosphere	water, deionised, at plant, CH	4.40E+0	kg	lognorm	4.5,nA,1,3,5	1.44	Estimation and from stoichiometric calcualtion
	sulphuric acid, liquid, at plant, RER	2.67E-1	kg	lognorm	4.5,nA,2,3,5	1.44	From stoichiometric calcualtion
	polystyrene, general purpose, GPPS, at plant, RER	3.08E-1	kg	lognorm	4.5,nA,2,5,5	2.15	From stoichiometric calcualtion, Proxy used
	electricity, medium voltage, at grid, CH	3.33E-1	kWh	lognorm	5.5,1,2,4,5	1.88	Approximation with data of a large chem. plant
	natural gas, burned in industrial furnace >100kW, RE	2.00E+0	MJ	lognorm	5.5,1,2,4,5	1.88	Approximation with data of a large chem. plant
	chemical plant, organics, RER	4.00E-10	unit	lognorm	5.5,1,2,4,5	3.55	Approximation with average chem. plant
	disposal, polystyrene, 0.2% water, to municipal incine	1.50E-2	kg	lognorm	5.5,nA,1,3,5	1.68	Calculated from estimated yield
	transport, freight, rail, RER	2.22E-1	tkm	lognorm	4.5,nA,nA,nA,nA	2.09	Estimated with standard distances
	transport, lorry 28t, CH	2.90E-2	tkm	lognorm	4.5,nA,nA,nA,nA	2.09	Estimated with standard distances
	Heat, waste, to air, high population density	1.20E+0	MJ	lognorm	5.5,1,2,4,5	1.88	Calculated from electricity demand
(1)	Sulfate, to water, river	1.30E-2	kg	lognorm	5.5,nA,1,3,5	3.36	Calculated from estimated yield
	(1) Emissions						

Tab. 93.12 In- / outputs for the module “anionic resin, at plant”, location CH

Process output: 1 kg, anionic resin, at plant, CH			Uncertainty			Comment
	Name, Location	Value	Unit	Type	Score	
From technosphere	water, deionised, at plant, CH	5.00E+0	kg	lognorm	4,5,nA,1,3,5	1.44 Estimation and from stoichiometric calcualtion
	dichloromethane, at plant, RER	2.35E-1	kg	lognorm	5,5,1,2,4,5	1.88 Estimated from a laboratory process
	chloromethyl methyl ether, at plant, RER	1.92E-1	kg	lognorm	4,5,nA,2,3,5	1.44 From stoichiometric calcualtion
	trimethylamine, at plant, RER	1.41E-1	kg	lognorm	4,5,nA,2,3,5	1.44 From stoichiometric calcualtion
	polystyrene, general purpose, GPPS, at plant, RER	2.70E-1	kg	lognorm	4,5,nA,2,5,5	2.15 From stoichiometric calcualtion, Proxy used
	electricity, medium voltage, at grid, CH	3.33E-1	kWh	lognorm	5,5,1,2,4,5	1.88 Approximation with data of a large chem. plant
	natural gas, burned in industrial furnace >100kW, RE	6.30E+0	MJ	lognorm	5,5,1,2,4,5	1.88 Approximation with data of a large chem. plant
	chemical plant, organics, RER	4.00E-10	unit	lognorm	5,5,1,2,4,5	3.55 Approximation with average chem. plant
	disposal, polystyrene, 0.2% water, to municipal incine	1.30E-2	kg	lognorm	5,5,nA,1,3,5	1.68 Calculated from estimated yield
	disposal, solvents mixture, 16.5% water, to hazardou	3.88E-1	kg	lognorm	5,5,nA,2,5,5	2.33 Estimated from solvent demand, Proxy used
Transport	transport, freight, rail, RER	3.95E-1	tkm	lognorm	4,5,nA,nA,nA,nA	2.09 Estimated with standard distances
	transport, lorry 28t, CH	4.60E-2	tkm	lognorm	4,5,nA,nA,nA,nA	2.09 Estimated with standard distances
	Heat, waste, to air, high population density	1.20E+0	MJ	lognorm	5,5,1,2,4,5	1.88 Calculated from electricity demand
1) Emissions						

93.10 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

93.11 Conclusions

The production of deionised water is determined largely by the raw water quality, the product water requirements, the plant design and the plant operation. Depending on the application of the deionised water there is a wide range of possible plant operation schemes. This makes it difficult to define an “average” plant operation. For further precision of the data it would be necessary to specify the raw- and product-water quality narrower and to have different processes for the different applications.

There is large uncertainty within the data of the plant infrastructure and the production of the ion exchange resins. Further investigations would be necessary to improve this data.

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94 White spirit

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94.1 Introduction

According to IPCS (1996) is white spirit a clear colourless solvent with very low water solubility and a characteristic odour.

The most common variety of white spirit is therefore a mixture of saturated aliphatic and alicyclic C₇-C₁₂ hydrocarbons with a content of 15-20% (by weight) of aromatic C₇-C₁₂ hydrocarbons and a boiling range of 130-230 °C. This ordinary white spirit is designated white spirit, type 1, regular grade, as three different types and three different grades exist (see Tab. 94.1).

Tab. 94.1 The different types and grades of white spirit (according to IPCS (1996))

Type of white spirit	Grade of white spirit
type 1 : Subject to hydrodesulphurization	low flash : flash point: 21-30 °C; initial boiling point: 130-144 °C
type 2 : Subject to solvent extraction	regular : flash point: 31-54 °C; initial boiling point: 145-174 °C
type 3 : Subject to hydrogenation	high flash : flash point: 55 °C; initial boiling point: 175-200 °C

The grade is thereby determined by the crude oil used as the starting material and the conditions of distillation. Furthermore, "Type 0" white spirit is defined as the distillation fraction with no further treatment, consisting predominantly of saturated C₉-C₁₂ hydrocarbons (boiling range 140-220 °C).

94.2 Reserves and Resources of material

White spirit is a fraction of petroleum and therefore all further discussion about reserves and resources can be found in the respective chapter about oil (see Dones et al. (2003)).

94.3 Use of material / product

IPCS (1996) indicates that white spirit is used as an extraction solvent, but also as cleaning, degreasing, aerosol solvent or in paints, wood preservatives and laquers, varnishes and asphalt products. According to Stoye (2000), white spirit is predominantly used in the paint industry as a solvent or diluent for oil-based, alkyd resin, chlorinated rubber and some vinyl chloride copolymers paints. According to IPCS (1996) these applications are responsible for more than 60% of the total white spirit consumption in Western Europe.

In 1985, the production of white spirit in the United States was in the order of 922 kt. Thereof, 236 kt were odourless white spirit, 324 kt Stoddard solvent and the remaining 326 kt 140 flash solvent (IPCS (1996)). There are no numbers given for other areas of the world.

94.4 Systems characterization

According to IPCS (1996) are the various types and grades of white spirit produced from naphtha and kerosene. These fractions are therefore subjected to fractional distillation into appropriate boiling ranges and to different kinds of treatments to obtain the desired type of white spirit. The composition of the solvents may vary due to variation in the composition of the crude oil and also because of the differences in refinery processing. White spirit may, therefore, have changed over time because of changes in manufacturing processes.

In this study, a distillation step as well as some subsequent treatment steps are assumed for white spirit. The functional unit is 1 kg of liquid white spirit and the location is RER.

94.5 White spirit, at plant (Location: RER)

This dataset includes a rough estimation of the production process for white spirit. Due to missing production data this inventory bases on theoretical reflections. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site (Gendorf (2000)). Due to these approximations the uncertainty within the results of this inventory is large.

The following assumptions and estimations are used here for the dataset of white spirit:

- **Energy:** There was no information available on the amount of energy used for the production process. In order not to neglect the process energy demand those values were approximated with data from a large chemical plant site in Germany producing 2.05 Mt a^{-1} (intermediates included) of different chemicals (Gendorf (2000)). The values for the energy consumption per kg of product of this plant (3.2 MJ kg^{-1}) were used as approximation for of the energy consumption of the white spirit production. This total energy demand contains a split of 50% natural gas, 38% electricity and 12% steam from external energy sources. For this inventory all energy used for heat or steam was assumed to be natural gas. For this inventory an amount of 2 MJ kg^{-1} natural gas and 1.2 MJ kg^{-1} electricity was used.
- **Raw material:** According to the information above, naphtha is used here. Due to missing quantitative informations, it is in a first approximation assumed here that 75% of the input have the correct chain length and are recovered in the distillation step. The other way round it means, that 1.333 kg naphtha are used per kg of white spirit and that the remaining 0.333 kg are accounted for as by-products (products not being within the specifications of the respective white spirit produced).
- **Transport and Infrastructure:** For the transports it is assumed that these plants are in the neighbourhood of traditional refineries and therefore, no transport amounts have to be accounted for. For the infrastructure of the production plant no information was available. It was assumed that the importance of the infrastructure is low and thus the module “chemical plant, organics” was used as approximation. For this module with a production capacity of 50'000 t per year and a plant life time of 50 years, an amount of $4 * 10^{-10}$ units per kg white spirit was included.
- **Waste heat:** It was assumed, that 100% of the electricity consumed, i.e. 1.2 MJ per kg white spirit is converted to waste heat. It was assumed that 100% of the waste heat is released to the air.
- **Emissions to air:** There was no data available on process emissions to air for the production of white spirit. As approximation the air emissions are estimated as 1% of different hydrocarbons – expressed as unspecified hydrocarbons.
- **Emissions to water:** There was no information available about emissions to water. As the process has no process water input, it is assumed here that no emissions to water occur.
- **Solid wastes:** Solid wastes occurring during the production of lubricants were neglected in this inventory.

94.6 Data quality considerations

The following table shows the data quality indicators as well as the inventory of the white spirit production (Location RER). The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The data in the inventory of the white spirit production has a high uncertainty, because only few data of the production processes were available. Further uncertainty occurs from possibly missing auxiliary

materials and further emissions or wastes. Smaller uncertainties are given for the raw material demand because it is only dependant on the yield-factor used for the stoicheometric calculations. Also for the infrastructure only an approximation was used because of missing data. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 94.9.

Tab. 94.2 Input / Output and uncertainty for the process “white spirit, at plant (RER)”

Explanation	Name	Location	Unit	white spirit, at plant		uncertaintyType standardDeviation95%	GeneralComment		
				RER					
				o	kg				
Input from Technosphere	naphtha, at refinery	RER	kg	1.33E+00	1	1.21	(4,na,na,na,na,na); estimation based on process yield 70 - 80%		
	electricity, medium voltage, production UCTE, at grid	UCTE	kWh	3.33E-01	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	heat, natural gas, at industrial furnace >100kW	RER	MJ	2.00E+00	1	1.88	(5,5,1,1,4,5); estimated with data from a large chem. plant		
	chemical plant, organics	RER	unit	4.00E-10	1	3.77	(4,5,1,3,5,4); estimation		
Output Air emission	white spirit, at plant	RER	kg	1					
	Heat, waste		MJ	1.20E+00	1	1.88	(5,5,1,1,4,5); calculated from electricity input		
	NMVOCS, non-methane volatile organic compounds, unspecified origin		kg	1.00E-02	1	2.32	(5,5,na,na,na,5); estimation		

94.7 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

94.8 Conclusions

The inventory for white spirit is based on a general literature source (Ullmann), estimations and assumptions. The unit process raw data are meant to be used as background information if white spirit is used for a product in small amounts. Therefore these data can only give an approximation. They are not reliable enough for direct comparison of this material with other, alternative products.

94.9 EcoSpold Meta Information

ReferenceFunction	401	Name	white spirit, at plant
Geography	662	Location	RER
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	402	IncludedProcesses	Raw materials and chemicals used for production, transport of materials to manufacturing plant, estimated emissions to air and water from production (incomplete), estimation of energy demand and infrastructure of the plant (approximation). Solid wastes omitted.
ReferenceFunction	404	Amount	1
ReferenceFunction	490	LocalName	Reinbenzin, ab Werk
ReferenceFunction	491	Synonyms	
ReferenceFunction	492	GeneralComment	The functional unit represent 1 kg of pure liquid white spirit. Large uncertainty of the process data due to weak data on the production process and missing data on process emissions.
ReferenceFunction	502	CASNumber	
TimePeriod	601	StartDate	2000
TimePeriod	602	EndDate	2000
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	date of published literature
Geography	663	Text	Data used has no specific geographical origin (stoichiometry). Average european processes for raw materials, transport requirements and electricity mix used.
Technology	692	Text	Production out of naphtha by fractional distillation into appropriate boiling ranges and followed by different kind of treatments to obtain the desired type of white spirit. The overall process yield is assumed to be 75%. Inventory bases on theoretical reflexions. The emissions to air are rough estimates.
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	
Representativeness	725	SamplingProcedure	Process data based on stoichiometric calculations of few literature sources. Energy demand based on approximation from large chemical plant. Process emissions based on estimations only.
Representativeness	726	Extrapolations	
Representativeness	727	UncertaintyAdjustments	none

94.10 References

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95 Xenon, Krypton

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 Review: Roland Hischier, EMPA St. Gallen

95.1 Introduction

The concentrations of krypton and xenon in the air are very small. Therefore, they are often neglected within the composition of air. Krypton (Kr) constitutes 0.00011 vol.-% of the air and xenon (Xe) constitutes 0.000008 vol.-% of the air. Xenon is an odourless, tasteless, colourless gas under the ordinary conditions.

The demand for xenon and krypton is growing due to new applications for these gases. Essentially the entire supply of xenon and krypton is produced by cryogenic fractional distillation of air. The most important physical properties of dry air, xenon and krypton used in this inventory are given in the following table. For the xenon krypton purification process the functional unit is 1 kg of gaseous xenon-krypton mixture in this inventory. For the allocated products the functional unit is 1 kg of gaseous xenon and 1 kg of gaseous krypton respectively.

Tab. 95.1 Physical properties of dry air, krypton and xenon

Property	Unit	Air	Xenon	Krypton
Molecular weight	g mol ⁻¹	28.96	131.3	83.7
Specific gravity ¹	kg Nm ⁻³	1.293	5.86	3.74
Normal boiling point	K	78.9	165.0	119.8
Specific gravity ²	kg m ⁻³	874	2945	2413
Amount in dry air ³	vol.-%	100	8 * 10 ⁻⁶	110 * 10 ⁻⁶

¹ At 273.15 K and 0.1013 MPa (Gieck 1995)

² At normal boiling point (Messer 2002)

³ Data source: (Flynn 1997)

95.2 Reserves and resources of material

Xenon and krypton are present in the atmosphere, which is the major source of its industrial production. The world production of xenon in 1998 was estimated to about 30-40 t per year (Ullmann 2002). The production of krypton is about 10 times larger (300-400 t per year). Xenon and krypton are produced in a purity of 99.99% (Messer 2002). In spite of very low concentrations of xenon in atmosphere, its mixture with krypton is produced at large air separation plants.

The assessment of the process for Europe gives an uncertainty within the relevant electricity mix. For the unspecified location in Europe (location: RER) the UCTE production mix was used. For specific locations, the use of regional supply mixes can lead to large differences in impact due to the different electricity production.

95.3 Use of material / product

Krypton and Xenon are used as filler gases for light bulbs or gas-discharge lamps. Further use of the two gases is as filler gas within the production of high insulating windows. Xenon is also used for particle detectors called bubble chambers, laser components and medicinal applications (anaesthesia).

95.4 Systems characterization

The production of xenon and krypton from air was assessed by the process of cryogenic air separation, where a xenon-krypton concentrate is derived, which is purified and concentrated to pure xenon and krypton. The process chain was assessed as shown in the figure below.

The following processes were modelled:

- Xenon krypton purification process (location: RER)
- Allocation of gaseous xenon, at plant (location: RER) and gaseous krypton, at plant (location: RER)
- Transport to Switzerland: Xenon, gaseous, at regional storage (location: CH) and krypton, gaseous, at regional storage (location: CH)

For this process, electricity as process energy is needed. As main resources, xenon and krypton from the air were accounted. A resource of minor importance is cooling water.

As output of the concentration and purification process there are the two products gaseous xenon and gaseous krypton.

Emissions to the air are already included in the preceding processes, especially in the electricity production, and are therefore not considered here. The only source of waste heat considered is the used electricity. As wastewater, there is the unevaporated share of the replaced cooling water, but it was not accounted because only minor emissions from this source were expected.

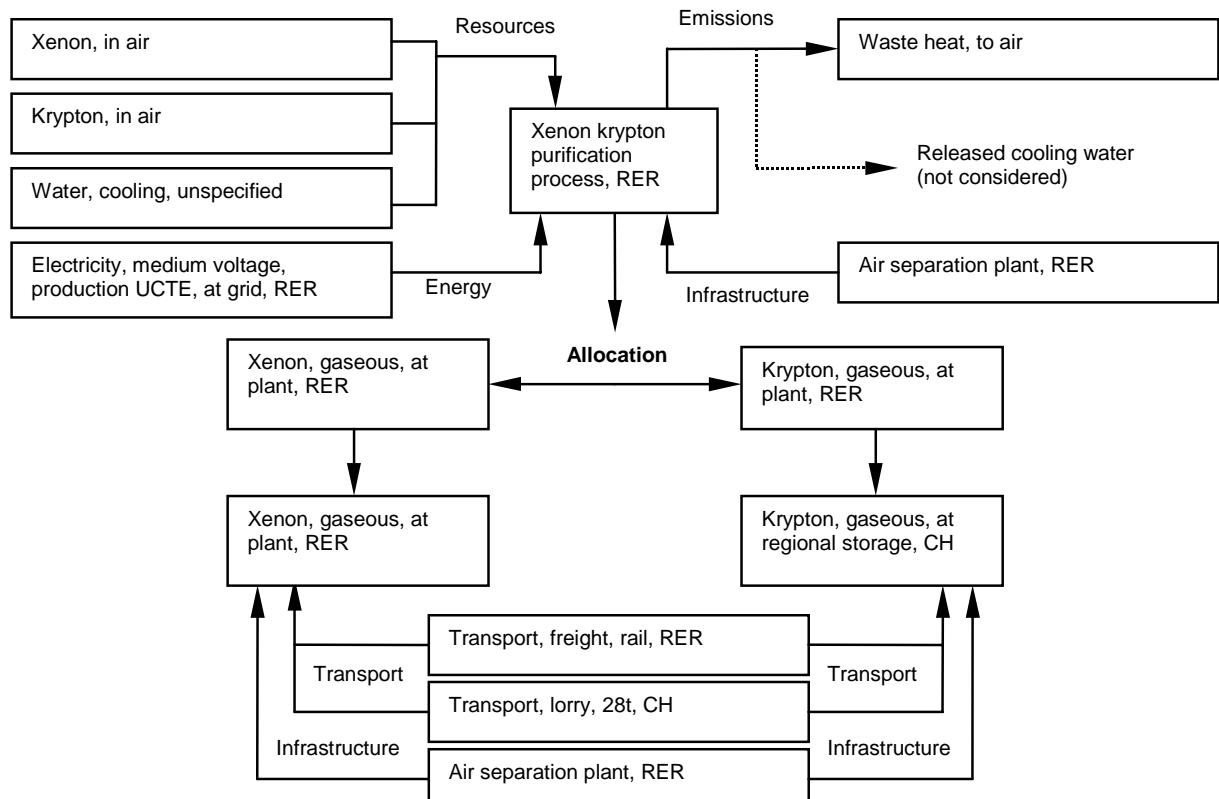


Fig. 95.1 Process chain for the production of liquid oxygen, liquid nitrogen and liquid argon

95.5 Xenon krypton purification process

95.5.1 Process

In a side column of large air separation plants a Kr-Xe-concentrate can be obtained with a concentration of about 0.2 vol.-% Kr and 0.015 vol.-% Xe. The rest of the concentrate contains mainly oxygen (99.4 vol.-%), argon and hydrocarbons (Ullmann 2002). Before the removal of these hydrocarbons there is no further concentration possible due to safety reasons (ignition limit). In a further crude krypton-xenon column consisting of a reactor, heater, flash vaporiser, liquid oxygen pump, and a purification column the concentration of the Kr-Xe mixture is increased to 85-92 vol.-% Kr and 6-12 vol.-% Xe. The rest of the mixture contains oxygen, nitrogen, argon and other trace gases (Hiller 2002). In a final laboratory scale purification and separation step, the pure gases are produced.

Most of the energy used for the process is needed due to the low Xe/Kr concentration in the concentrate (0.2 vol.-% Xe/Kr). This means that a large volume has to be processed to obtain 1 Nm³ of krypton or xenon. A large amount of oxygen in the concentrate needs to be evaporated (distilled) and returned to the concentration step. This leads to an exergy loss of this gas stream due to the vaporisation-liquefaction-cycle.

An important value is the Xe-Kr yield obtained by the concentration and purification steps. According to Weir & Muneer 1998 the yield lies between 31-54% with an average of 42%. A plant producing 50'000 Nm³ oxygen per hour can produce 100 Nm³ of pure xenon (Ullmann 2002). This is equal to a yield for xenon of nearly 60%. This yield is of high importance for the value calculated for the specific energy demand of the process. The following figure gives a simplified scheme of the xenon krypton production process:

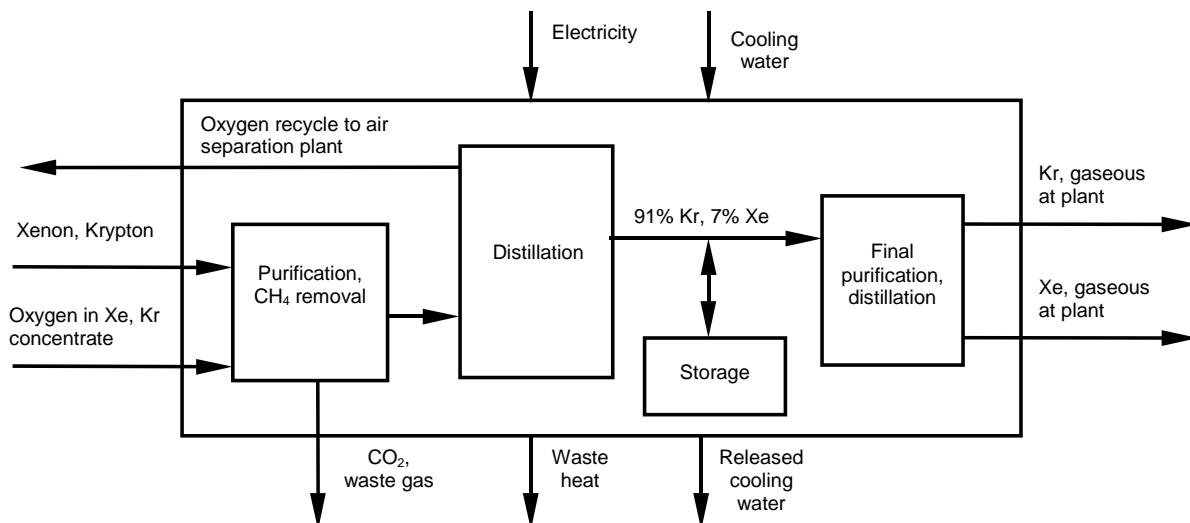


Fig. 95.2 Simplified process of the xenon krypton purification process

95.5.2 Resources

Xenon, Krypton

Due to their small amount in air and the possibility for scarcity, the xenon and krypton were accounted as resource from air. It was assumed that all loss of yield during the production would be released back to the atmosphere. Therefore only the xenon and krypton in the product was accounted. For this inventory a value of 0.105 kg xenon and 0.895 kg krypton were accounted per kg Xe-Kr mixture produced.

Electricity

The xenon krypton purification process requires large quantities of electricity, because of the low amount of xenon and krypton obtained directly from the side columns of the air separation plant. According to data presented in Binz et al. 2000, an amount of 800 kWh Nm⁻³ is needed for krypton (2483 MJ per kg krypton as primary energy for UCTE production mix) and 8500 kWh Nm⁻³ for xenon (16'835 MJ per kg xenon as primary energy for UCTE production mix). These data represent an average production process in Western Europe. For the mixture obtained from the concentration and purification step, an energy demand of 1341 kWh Nm⁻³ of the Xe-Kr mixture was calculated. For this calculation a composition of 91.3 vol.-% Kr and 6.9 vol.-% Xe for the Kr-Xe mixture was applied as obtained in a large separation plant presented in Weir & Muneer 1998. Only the shares of xenon and krypton were considered in the calculation because the other components in the gas (1.8 vol.-%; Hydrocarbons, O₂, N₂, Ar) are removed and not further used.

In an analysis of the gas production process in Weir & Muneer 1998 the power rating of the equipment used for the Xe-Kr concentration and purification step was given with 23.5 kW. This value includes a reactor (4 kW), heater (10.8 kW), flash vaporiser (4 kW), liquid oxygen pump (2.3 kW) and the purification column (2.4 kW). With this equipment an amount of 0.047 Nm³ h⁻¹ of Xe-Kr-mixture is obtained. From these data an energy demand for equipment of 500 kWh Nm⁻³ of the Xe-Kr mixture was calculated.

For the oxygen used within the process, only the exergy loss of the vaporisation- liquefaction-cycle has to be taken into account. The oxygen gas recycled after the separation of xenon and krypton (distillation) is used for further processing and is not to be accounted as waste gas. According to Cornelissen & Hirs 1998 the liquefaction unit of an air separation plant has an energy demand of 6470 kWh to obtain 13.3 t of liquid products (O₂, N₂, Ar). Calculating with an average density of 1.293 kg Nm⁻³ (gaseous), an energy demand for liquefaction of 0.63 kWh Nm⁻³ is obtained. This amount was applied to 1110 Nm³ oxygen used to process 1 Nm³ Xe-Kr-mixture from the concentrate (0.215 vol.-% Xe-Kr) with an average Xe-Kr efficiency of 42%. This leads to additional 700 kWh energy needed per Nm³ of the Xe-Kr mixture. With the energy demand for the equipment a total energy demand (equipment + oxygen liquefaction) of 1200 kWh per Nm³ of Xe-Kr mixture was calculated. This value does not yet include the final purification and separation steps to obtain the final products. Therefore the value for the final product will be higher.

The yield within the process is an important factor for the energy needed. If the range of yields reported by Weir & Muneer 1998 of 31-54% is applied on the above calculation an energy demand between 1043 kWh and 1445 kWh per Nm³ of the Xe-Kr mixture is obtained. For this inventory the value of 1341 kWh per Nm³ of Xe-Kr mixture given by Binz et al. 2000 was applied because it represents an average production process. Calculated with an average density of the mixture of 3.89 kg Nm⁻³ (93 vol.-% Xe and 7 vol.-% Kr), an energy demand of 345 kWh per kg of the Xe-Kr mixture is obtained. It was assumed that all energy used for this process is electricity. A summary of the values used is given in Tab. 95.2.

Cooling water

The main cooling circuit is connected with that of the air separation plant. It was assumed that there is an open re-circulating system with a cooling tower installed. There will be need for replacement of water due to evaporation and blowdown. According to IPPC 2000 the demand for make up water is about 2 kg h⁻¹ for a cooling demand of 1 kW. According to Recknagel et al. 1997 (p. 1805) a maximal cooling water make up of 3 kg h⁻¹ is necessary to cool 1 kW of generated waste heat. A cooling water make up of 0.7⁻¹ m³ per kg of Xe-Kr mixture was calculated assuming an average produced waste heat of 345 kWh per kg of the Xe-Kr mixture. For this inventory a value of 0.7 m³ cooling water per kg of Xe-Kr mixture was used.

95.5.3 Emissions

Waste heat

It was assumed, that 100% of the electricity consumed is converted to waste heat, which amounts to 1242 MJ per kg of Xe-Kr mixture produced. It was assumed that 100% of the waste heat is released to the air, mainly through evaporation in the cooling tower.

Emissions to air

The released waste gas contains the non-extracted impurities of the air (mainly N₂, Ar, hydrocarbons and CO₂ from the catalytic oxidation). Due to the small amount of hydrocarbons oxidised, those emissions were neglected. The other waste gases are unchanged components of the air feed and therefore not considered. There are no other emissions to the air considered. The main source of air emissions lies within the electricity production process.

Wastewater

From the input of cooling water the unevaporated part is released again as wastewater. According to the assumptions for the cooling water about 33% of the cooling water make up will be lost due to spray losses (Recknagel et al. 1997, p. 1805). The other 67% will evaporate in the cooling tower. This means that 0.233 kg water per kg of liquefied product will leave the cooling system as wastewater. In this wastewater small amounts of treatment chemicals used for scaling- and fouling inhibition are present. The water pollution due to the use of these chemicals was not considered in this inventory.

Tab. 95.2 Energy demand, resource demand and emissions for production of xenon- / krypton.

Resource, emission	Unit	per kg xenon- krypton mixture
Xenon, in air	kg	0.105
Krypton, in air	kg	0.895
Electricity, medium voltage, production UCTE, at grid	kWh	345 ¹
Water, cooling, unspecified natural origin	m ³	0.7
Waste heat to air ²	kg	1242
Cooling water vapour to air ³	kg	467
Waste water from cooling ³	kg	233

¹ Value for an average process (Binz et al. 2000). Calculated for a mixture of 93 vol.-% krypton and 7 vol.-% xenon.

² Only waste heat from electricity use considered. Waste heat from reaction in preceding processes considered.

³ Not considered in the inventory. Emissions to water from released cooling water neglected.

95.5.4 Infrastructure

The infrastructure needed for the production of xenon and krypton consists of the concentration and purification column in the air separation plant. For the further purification and separation of the two gases, additional infrastructure such as a catalytic purifying systems and a further distillation column is needed. Within these purifying systems, catalyst (e.g. platinum, copper or magnesium) and getter systems (e.g. active carbon) are used. There was no information available on the composition and amount of these components, and they were neglected in the present work. Neither was information on the infrastructure demand of the whole process available. Due to this lack of information the infrastructure of the process was assessed by using the volume of oxygen processed to produce 1 Nm³ of

xenon-krypton mixture as indicator. With this indicator the amount of infrastructure used within the air separation plant was calculated.

Per 1 Nm³ Xe-Kr-product an amount of 1110 Nm³ O₂ is needed assuming a yield of 42 vol.-% and an input concentration of 0.215 vol-% Xe-Kr. This leads to an amount of 408 kg O₂ to produce 1 kg Xe-Kr-product (density: 3.89 kg Nm⁻³). According to the assessment of the infrastructure for the air separation process, $0.7 * 10^{-6}$ units per kg of liquefied O₂ are needed. This value refers to a plant with an annual production of 80'000 t liquid product and a lifetime of 20 years. This leads to an amount of $0.25 * 10^{-6}$ units per kg of Xe-Kr-product for the infrastructure share of the Xe-Kr concentration within the air separation plant.

Because additional infrastructure is needed besides the equipment within the air separation plant for purifying and separating the xenon-krypton mixture, the calculated value was doubled assuming a similar amount of infrastructure for this further process step. This leads to an amount of $0.5 * 10^{-6}$ units per kg of Xe-Kr-product for the total infrastructure of the Xe-Kr production. For a large air separation plant (50'000 Nm³ oxygen per hour) producing 550 kg xenon and 5500 kg krypton per year, infrastructure amounts to 6 t of material, which seems reasonable.

95.6 Allocated products of xenon krypton purification

An important step in the process chain is the allocation of the burdens on to the products “krypton, gaseous, at plant” and “xenon, gaseous, at plant”. For this allocation an allocation method according to the sales price was chosen.

The energy used within the concentration and purification of the xenon-krypton mixture is an important parameter, which should be used for allocation. Because no detailed energetic analysis of the production process was available these values could not be used directly for allocation. Therefore, the price was taken as allocation factor, which seems to represent the energy use most accurately because of the high-energy costs within this process.

According to Ullmann 2002, the price for small quantities of krypton was approximately 1000 Euro per Nm³ in Europe (1999). The price for xenon is reported with 10'000 Euro per Nm³. Calculated for an output of 93 vol.-% Xe and 7 vol.-% Kr this leads to a price of 10'000 Euro per kg of the Xe-Kr-mixture. With this allocation the energy demand for the production of 1 kg krypton was calculated to 220 kWh and for the production of 1 kg xenon to 1404 kWh. The applied allocation factors are presented here.

Tab. 95.3 Calculated allocation factors for xenon-krypton production. Allocation to gaseous xenon and krypton.

Product gas	Cost of product ¹	Density	Process output	Cost per output	Allocation factor ²	Allocated energy consumption ³
	Euro Nm ⁻³	kg Nm ⁻³	kg	Euro	%	kWh kg ⁻¹
Xenon	10000	5.860	0.105	180	42.9	1404
Krypton	1000	3.740	0.895	239	57.1	220
Total	-	-	1.000	419	100.0	345

Process output according to concentration in the xenon-krypton mixture obtained (93 vol.-% Kr, 7 vol.-% Xe).

¹ Sales prices for small quantities in Europe (1999). Source: (Ullmann 2002)

² Referenced to assumed process output.

³ Calculated as allocated energy demand per 1kg of gaseous output.

Similar allocation factors would be obtained if the amount of oxygen in the process cycle needed to produce 1 kg of xenon or 1 kg krypton would be used as indicator. The amount of oxygen used in the process cycle is also an indicator for the energy used (liquefaction of O₂).

The allocation described in the table above was not applied for the resources xenon and krypton. These resources were allocated to 100% to the corresponding product.

95.7 Xenon / krypton, gaseous, at regional storage

95.7.1 Process and requirements

There is no production of xenon and krypton in Switzerland, because the large air separation plants where xenon and krypton can be produced commercially are located in vicinity of industrial complexes where gaseous oxygen and nitrogen products are used in large quantities (e.g. steel industry).

Xenon and krypton are transported in steel cylinders comparable to those used for other gaseous products. These cylinders have 50 l volume and the gas is filled with 20 MPa overpressure (Ullmann 2002). For smaller amounts cylinders with 6 MPa overpressure and 0.1 Nm³ to 2 Nm³ gas content are common (Messer 2002). Air separation plants with xenon and krypton production are located in France and in Germany as well as in Russia. There was no survey available to calculate actual distances for an average consumption in Switzerland. For this inventory the standard distances for steel used in this project were applied (600 km rail, 50 km road), assuming that the distances are similar, because steel plants use large quantities of oxygen. In order to include the weight of the transported steel cylinder, the double weight was used for the calculation of the transport needs. This leads to 1.2 tkm rail transport and 0.1 tkm road transport (28 t lorry) per kg of gaseous product.

95.7.2 Infrastructure

The infrastructure of the regional storage facilities was only roughly estimated. It was assumed that for the storage of the gases about 1-5 m³ storage volume or 0.3-3 m² floor area is needed per ton of product. For this inventory an amount of 1 m² floor area per ton of product was used.

The infrastructure used in this inventory refers to a storage building for solid chemicals (as. e.g. sodium chloride). As an approximation for the infrastructure demand (building infrastructure) this module was nevertheless used. The storage site assessed includes a total floor area of 6'000 m². To calculate the amount of infrastructure needed, the average storage time should be known. There was no information on this value available. As estimation, a storage time of 2 month was assumed. For the time of occupation of the building, 50 years were assumed. This leads to a total amount of stored product during the operation time of 1.8 Mt or $5 * 10^{-10}$ units per kg of product. In the following a summary of the values used is given:

Tab. 95.4 Resources for regional storage of gaseous xenon and krypton

Resource, emission	Unit	per kg xenon, gaseous	per kg krypton, gaseous
Xenon, gaseous, at plant	kg	1	
Krypton, gaseous, at plant	kg		1
Transport, freight, rail, RER	tkm	1.2	1.2
Transport, lorry 28t, CH	tkm	0.1	0.1
Storage building, chemicals, solid	unit	$5 * 10^{-10}$	$5 * 10^{-10}$

²Waste heat from electricity use and burned hydrogen.

95.8 Data quality considerations

Tab. 95.5 shows the data quality indicators for the inventory of the xenon krypton purification process. In Tab. 95.7 and Tab. 95.8, data quality indicators are shown for the inventory of gaseous xenon at regional storage and gaseous krypton at regional storage respectively. The uncertainty scores include reliability, completeness, temporal correlation, geographical correlation, further technological correlation and sample size.

The most important data for the production of xenon and krypton is the electricity demand. However, the electricity demand is uncertain because there are different production paths and also the yield and therefore the specific energy demand of product may vary. It is not known how representative the data are. The used electricity mix refers to an average European production. Therefore, for a specific location of the air separation plant, large differences may occur when using a local supply mix.

The allocation used is based on the economic situation in 1998. Due to rising demand of noble gases the prices might change. The uncertainty in using this allocation rule is of importance but cannot be quoted as a data uncertainty. The allocated values for the two gases are shown in Tab. 95.6.

The cooling water demand is based on assumptions concerning the operation of the cooling circuit and has therefore high uncertainties. The use and replacement of catalysts and used absorber materials was not considered in this inventory due to missing data. The uncertainty of those missing data could not be considered within this uncertainty assessment.

In general the infrastructure data has a high uncertainty because due to missing process specific information the infrastructure was assessed with the same infrastructure module as the separation plant itself. Due to the high electricity use of the whole process this inaccuracy might be of minor importance. The modules for the regional storage are only rough estimations, but they may help to see the importance of those transportation processes.

Tab. 95.5 In- / outputs for the module “xenon krypton purification process”, location RER

Process output: 1 kg, xenon krypton purification process, RER					Comment
Name, Location	Value	Unit	Type	Score	
electricity, medium voltage, production UCTE, at grid, UCT	3.45E+2	kWh	lognorm	3,4,1,1,1,5	1.26E+0 Data from an average process, estimations
air separation plant, RER	5.00E-7	unit	lognorm	5,5,1,3,5,5	4.00E+0 Estimated
Water, cooling, unspecified natural origin	7.00E-1	m3	lognorm	3,4,1,1,4,5	1.60E+0 Assumptions of technology used for cooling
Xenon, in air	1.05E-1	kg	lognorm	nA,nA,nA,nA,nA,nA	1.05E+0 Ressource input determined from output
Krypton, in air	8.95E-1	kg	lognorm	nA,nA,nA,nA,nA,nA	1.05E+0 Ressource input determined from output
Heat, waste, to air, low population density	1.24E+3	MJ	lognorm	3,4,1,1,1,5	1.26E+0 Calculated from electricity use
xenon, gaseous, at plant, RER	1.05E-1	kg	-	not applicable	- Uncertainty not applicable for allocated product
krypton, gaseous, at plant, RER	8.95E-1	kg	-	not applicable	- Uncertainty not applicable for allocated product

(1) From technosphere; (2) Ressources; (3) Emissions; (4) Products of multi output process

Tab. 95.6 Allocation factors for the products “xenon, gaseous, at plant” and “krypton, gaseous, at plant”,

Allocation factors used for products of xenon krypton purification process: xenon, krypton; gaseous, at plant, RER			
Name, Location	Unit	Allocation factor used	Comment
electricity, medium voltage, production UCTE, at grid, UCT	%	42.9	57.1 Allocation with economic criteria (sales price)
air separation plant, RER	%	42.9	57.1 Allocation with economic criteria (sales price)
Water, cooling, unspecified natural origin	%	42.9	57.1 Allocation with economic criteria (sales price)
Xenon, in air	%	100.0	0.0 To 100% allocated to Xenon
Krypton, in air	%	0.0	100.0 To 100% allocated to Krypton
Heat, waste, to air, low population density	%	42.9	57.1 Allocation with economic criteria (sales price)
Allocated amount	kg	1.05E-1	8.95E-1 Product output with average composition

(1) From technosphere; (2) Ressources; (3) Emissions; (4) Product outputs of multi output process

Tab. 95.7 In- / outputs for the module “xenon, gaseous, at regional storage”, location CH

Process output: 1 kg, xenon, gaseous, at regional storage, CH		Value	Unit	Uncertainty			Comment
Name, Location	Type	Score	St.Dev.				
xenon, gaseous, at plant, RER	1.00E+0	kg	lognorm	nA,nA,nA,nA,nA	1.05E+0	Material input, Uncertainty set to 1.05	
transport, freight, rail, RER	1.20E+0	tkm	lognorm	4,5,1,1,4,5	2.37E+0	Estimated with standard distances for steel	
transport, lorry 28t, CH	1.00E-1	tkm	lognorm	4,5,1,1,4,5	2.37E+0	Estimated with standard distances for steel	
storage building, chemicals, solid, CH	5.00E-10	unit	lognorm	5,5,1,3,5,5	4.00E+0	Estimated	
1) From technosphere							

Tab. 95.8 In- / outputs for the module “krypton, gaseous, at regional storage”, location CH

Process output: 1 kg, krypton, gaseous, at regional storage, CH		Value	Unit	Uncertainty			Comment
Name, Location	Type	Score	St.Dev.				
krypton, gaseous, at plant, RER	1.00E+0	kg	lognorm	nA,nA,nA,nA,nA	1.05E+0	Material input, Uncertainty set to 1.05	
transport, freight, rail, RER	1.20E+0	tkm	lognorm	4,5,nA,nA,nA,nA	2.09E+0	Estimated with standard distances for steel	
transport, lorry 28t, CH	1.00E-1	tkm	lognorm	4,5,nA,nA,nA,nA	2.09E+0	Estimated with standard distances for steel	
storage building, chemicals, solid, CH	5.00E-10	unit	lognorm	5,5,1,3,5,5	4.00E+0	Estimated	
1) From technosphere							

95.9 Cumulative results and interpretation

Results of the cumulative inventory can be downloaded from the database.

95.10 Conclusions

For further precision of the data it would be necessary to assess the different processes used for purification more in detail and to determine a representative average for the product yield and the energy demand. Further, the infrastructure was included only as very rough estimate. If it turns out to be of some relevance the neglected catalysts and adsorption materials should be assessed. In future work a large separation plant should be assessed with all product paths (liquid and gaseous).

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96 Xylenes

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96.1 Introduction

This chapter describes the production of xylenes. These chemicals are available as one of three isomers – ortho-, meta- or paraxylol, depending on how the two methyl groups on the benzene ring are situated. Xylenes are used primarily for the improvement of gasoline octane.

Synonyms for xylenes: dimethylbenzene, dimethyl benzol, methyl toluene

96.2 Reserves and resources of xylenes

Xylenes are organic chemical compounds. They are produced from catalytic reforming of petroleum. Xylene production is almost always associated with the production of ethylbenzene.

96.3 Characterisation of xylenes

Xylenes are basically benzene rings with two methyl groups, chemical formula C₈H₁₀ or C₆H₄(CH₃)₂. There are three isomers, as mentioned above.

	Physical appearance	Molecular weight	Melting point (°C)	Boiling point (°C)
o-xylene	Colorless liquid	106.16	- 25.2	144.4
m-xylene	Colorless liquid	106.16	- 48	139
p-xylene	Colorless liquid or crystals	106.16	-13.3	138.4

All xylenes are flammable and toxic. They are soluble in ethyl alcohol but insoluble in water (Wells (1999)).

96.4 Production and use of xylenes

According to (European Commission (2002)), 85% of all xylenes in the US and Europe stem from reformate. The presence of ethylbenzene makes xylene isomer separation difficult because of the proximity of ethylbenzene's boiling point to that of m- and p-xylene. Another route of obtaining xylenes is from disproportionation of toluene to xylene, which does not entail the presence of ethylbenzene.

The most sought-after xylene is para-xylene, which is used for the production of polyethylene terephthalate (PET), o-Xylene is used for phthalic anhydride production, while m-xylene is used as solvents.

In 1997-2000, EU annual production of p-xylene was 1.4 million tons, while production of o-xylene is given as 0.7 million tons. No information is given on m-xylene. The growing use of PET has led to increased demand for p-xylene (European Commission (2002)).

Major o-xylene plants are located in the Netherlands, Germany, Russia, the US, South Korea and Japan. Major p-xylene plants are located in the UK, the US, Japan, South Korea, China (PRC), Singapore and Puerto Rico. Producers include Exxon Chemical, Deutsche Shell, LG-Caltex and Mobile Oil, among others.

96.5 System characterization

Xylene is produced from aromatic-rich streams from refineries or as a by-product of naphtha cracking. The resulting mixtures of benzene, toluene and xylenes (BTX streams) are then separated by a variety of means, including fractionation, crystallization and solid absorption.

96.5.1 p-Xylene, o-Xylene (Wells (1999))

Crystallization techniques take advantage of the spread of melting points to separate the xylene isomers. These processes usually are geared to producing p-xylene. The mixed xylene feed is dried and cooled. Crystals that form on tank walls are scraped and then centrifuged to p-xylene of about 85% purity. These crystals are then melted and recrystallized, so that p-xylene of 99% is obtained.

Where o-xylene is required, it can be separated from p-xylene by fractionation.

p-Xylene can also be recovered using solid absorption of the molecular-sieve type. By washing with a deabsorbant, p-xylene can be recovered by distillation. The absorbant and deabsorbant are reusable. A purity in excess of 99.5% is claimed.

Isomerization of C₈-streams: there are four different types of isomerization processes, each of which uses a different catalyst system. Isomerization uses a C₈ feed with little p-xylene in it (eg recycle stream, streams with ethylbenzene). The catalysts convert the feedstock to p- and o-xylene.

96.5.2 m-Xylene

m-Xylene can be recovered from the filtrate from p-xylene crystallization at up to 85% purity. m-Xylene can also be extracted from C₈ feed using a catalyst and fractionation, which leads to pure m-xylene.

96.5.3 Disproportionation and transalkylation of toluene

Toluene and C₉ aromatics can be transformed to benzene and xylene by several processes. These processes involve catalysts and varying reaction conditions. The major advantage of these routes is that the xylene produced contains hardly any ethylbenzene.



(1) Toluene is transformed to benzene and xylene

(2) Toluene and a C₉ hydrocarbon form xylenes

Energy usage and precursor materials

Tab. 96.1 Energy usage for and precursor materials for xylene production (European Commission (2002))

Consumption per ton of feedstock	Reformate plant
Fuel gas	3 – 10 kg
Steam (tons)	0.5 – 1.5
Electricity (MWh)	<0.07
Production (tons) per ton of feedstock	
p-xylene	0.23 – 0.48
o-xylene	0 – 0.25a

Air emissions

Little is given on toluene production alone as most information pertains to benzene or BTX production plants.

Tab. 96.2 Air emissions for toluene production (European Commission (2002))

Air pollutant (kg/ton product)	Methane	SO2	Particulates	VOC *	Methane
BTX from aromatic mixture (source: a single plant)	0.086	0.53	0.008 kg/ton feedstock	0.03 toluene 0.2 NMVOOctot*	0.09
Benzene from pyrolysis gas (source: a single plant)	0.013	0	0.0025 kg/ton feedstock	0.03**NMVOOctot	ng

* tanks and various fugitive sources, calculated according to table 8.9 (European Commission (2002))

** benzene: 0.010, toluene: 0.004, pentanes 0.004

Most VOC emissions are normally fugitive (valves, flanges) and from maintenance or inspections. They may also stem from small leaks in cooling systems as well as storage tank breathing losses and displacement.

Wastewater emissions

BTX production entails little or no continuous wastewater. The main source is process water or condensates of distillation towers that may contain small amounts of dissolved organics. The water is treated in a facility WWTP. There also may be some wastewater containing sulfides or COD.

Tab. 96.3 Wastewater from BTX production (European Commission (2002))

Pollutant (kg/ton product)	Benzene	Toluene	COD	N-Kjeldahl	Sulphide
BTX from aromatic mixture (source: a single plant)	0.003	0.001	0.087	0.0009*	ng
Benzene from pyrolysis gas (source: a single plant)	ng	ng	ng	ng	0.075

Liquid wastes

No liquid wastes are given.

Solid wastes

The wastes are usually recycled, landfilled or incinerated in a hazardous waste incinerator.

The main solid wastes are spent catalyst (from the hydrogenation process), clay from olefins removal, adsorbents from xylene separation and sludge recovered from process equipment. There are also oil-contaminated materials and sludges, which are incinerated with heat recovery. Amounts are given according to (European Commission (2002), Chapter 8.11)

Tab. 96.4 Solid wastes from BTX production (European Commission (2002))

Pollutant (kg/ton product)	Catalysts*	Clay, desiccant material, inert balls**	Activated carbon***	Filter cloth, „etc.“ ***
BTX from aromatic mixture (source: a single plant)	0.05	0.006	0.01	0.0009*
Benzene from pyrolysis gas (source: a single plant)	0.037	ng	ng	ng

* recycled via supplier

** reused after regeneration

*** incinerated

96.6 Life cycle Inventory for xylenes

The production process for xylenes was assessed with data from PlasticsEurope (Boustead (2005-07)), representing an average value from eleven European plants. Due to the fact that this dataset is cumulated it was not possible to use the other processes modelled in ecoinvent to obtain a transparent process chain. The data was nevertheless used because it represents a high share of the European production of this type of chemicals. The transformation for the data as given in Boustead (2005-07) to the data format in ecoinvent is described in detail in the methodology part of the plastics part in Hischier (2007).

Within the module assessed here there are only the resources and emissions considered which are given in the data source. Therefore no land use could be included and no direct soil emissions within the process chain are stated. For each waste type used in the original dataset, an appropriate waste process from the ecoinvent modules was included.

96.7 Data quality considerations

Tab. 96.5 to Tab. 96.7 summarize the resulting data of the xylenes production in Europe. According to the methodological remarks in Hischier (2007), these data contain no uncertainty information. Additionally, the most important fields of the ecospold meta information from this dataset are listed in chapter 96.10.

Tab. 96.5 Input data and functional unit outflow of the dataset for xylene production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	xylene, at plant	uncertaintyType	standardDeviations95%	GeneralComment
	662	Location		RER o			
	493	InfrastructureProcess		kg			
	403	Unit					
Resources		Oil, crude, in ground	kg	8.03E-01			Uncertainty for LCI results cannot be determined
		Gas, natural, in ground	Nm3	6.79E-01			Uncertainty for LCI results cannot be determined
		Coal, hard, unspecified, in ground	kg	5.57E-02			Uncertainty for LCI results cannot be determined
		Coal, brown, in ground	kg	3.13E-08			Uncertainty for LCI results cannot be determined
		Peat, in ground	kg	1.26E-04			Uncertainty for LCI results cannot be determined
		Wood, unspecified, standing	m3	3.27E-09			Uncertainty for LCI results cannot be determined
		Energy, potential (in hydropower reservoir), converted	MJ	7.37E-02			Uncertainty for LCI results cannot be determined
		Uranium, in ground	kg	3.13E-06			Uncertainty for LCI results cannot be determined
		Energy, gross calorific value, in biomass	MJ	1.21E-01			Uncertainty for LCI results cannot be determined
		Barite, 15% in crude ore, in ground	kg	3.14E-08			Uncertainty for LCI results cannot be determined
		Aluminium, 24% in bauxite, 11% in crude ore, in ground	kg	3.41E-07			Uncertainty for LCI results cannot be determined
		Clay, bentonite, in ground	kg	9.46E-05			Uncertainty for LCI results cannot be determined
		Anhydrite, in ground	kg	9.44E-06			Uncertainty for LCI results cannot be determined
		Calcite, in ground	kg	3.26E-04			Uncertainty for LCI results cannot be determined
		Clay, unspecified, in ground	kg	2.87E-10			Uncertainty for LCI results cannot be determined
		Chromium, 25.5% in chromite, 11.6% in crude ore, in ground	kg	1.77E-12			Uncertainty for LCI results cannot be determined
		Copper, 0.99% in sulfide, Cu 0.36% and Mo 8.2E-3% in crude ore, in ground	kg	1.09E-08			Uncertainty for LCI results cannot be determined
		Dolomite, in ground	kg	4.08E-06			Uncertainty for LCI results cannot be determined
		Iron, 46% in ore, 25% in crude ore, in ground	kg	3.32E-04			Uncertainty for LCI results cannot be determined
		Feldspar, in ground	kg	2.62E-16			Uncertainty for LCI results cannot be determined
		Manganese, 35.7% in sedimentary deposit, 14.2% in crude ore, in ground	kg	4.28E-07			Uncertainty for LCI results cannot be determined
		Fluorspar, 92%, in ground	kg	3.38E-07			Uncertainty for LCI results cannot be determined
		Granite, in ground	kg	1.94E-15			Uncertainty for LCI results cannot be determined
		Gravel, in ground	kg	1.23E-06			Uncertainty for LCI results cannot be determined
		Cinnabar, in ground	kg	7.02E-10			Uncertainty for LCI results cannot be determined
		Magnesite, 60% in crude ore, in ground	kg	2.54E-18			Uncertainty for LCI results cannot be determined
		Nickel, 1.98% in silicates, 1.04% in crude ore, in ground	kg	6.95E-13			Uncertainty for LCI results cannot be determined
		Olivine, in ground	kg	3.12E-06			Uncertainty for LCI results cannot be determined
		Lead, 5.0% in sulfide, Pb 3.0%, Zn, Ag, Cd, In, in ground	kg	2.13E-07			Uncertainty for LCI results cannot be determined
		Phosphorus, 18% in apatite, 12% in crude ore, in ground	kg	1.31E-12			Uncertainty for LCI results cannot be determined
		Sylvite, 25 % in sylvite, in ground	kg	4.98E-09			Uncertainty for LCI results cannot be determined
		TiO2, 95% in rutile, 0.40% in crude ore, in ground	kg	4.89E-34			Uncertainty for LCI results cannot be determined
		Sulfur, in ground	kg	7.54E-05			Uncertainty for LCI results cannot be determined
		Sand, unspecified, in ground	kg	1.05E-04			Uncertainty for LCI results cannot be determined
		Shale, in ground	kg	2.67E-05			Uncertainty for LCI results cannot be determined
		Sodium chloride, in ground	kg	4.22E-04			Uncertainty for LCI results cannot be determined
		sodium nitrate, in ground	kg	7.63E-18			Uncertainty for LCI results cannot be determined
		Talc, in ground	kg	1.24E-27			Uncertainty for LCI results cannot be determined
		Zinc, 9.0% in sulfide, Zn 5.3%, Pb, Ag, Cd, In, in ground	kg	7.78E-09			Uncertainty for LCI results cannot be determined
		Water, unspecified natural origin	m3	9.40E-04			Uncertainty for LCI results cannot be determined
		Water, river	m3	2.39E-04			Uncertainty for LCI results cannot be determined
		Water, salt, ocean	m3	5.23E-04			Uncertainty for LCI results cannot be determined
		Water, well, in ground	m3	1.05E-10			Uncertainty for LCI results cannot be determined
		Water, cooling, unspecified natural origin	m3	7.25E-02			Uncertainty for LCI results cannot be determined
Input from Technosphere		disposal, facilities, chemical production	kg	9.07E-05			Uncertainty for LCI results cannot be determined
		disposal, hard coal mining waste tailings, in surface backfill	kg	1.12E-02			Uncertainty for LCI results cannot be determined
		disposal, municipal solid waste, 22.9% water, to municipal incineration	kg	1.63E-03			Uncertainty for LCI results cannot be determined
		disposal, average incineration residue, 0% water, to residual material landfill	kg	5.08E-03			Uncertainty for LCI results cannot be determined
		disposal, wood untreated, 20% water, to municipal incineration	kg	4.30E-08			Uncertainty for LCI results cannot be determined
		disposal, plastics, mixture, 15.3% water, to municipal incineration	kg	6.54E-06			Uncertainty for LCI results cannot be determined
		disposal, hazardous waste, 0% water, to underground deposit	kg	1.88E-03			Uncertainty for LCI results cannot be determined
Output		xylenes, at plant	kg	1.00E+00			

Tab. 96.6 Emission to air data for xylene production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	xylene, at plant	standardDeviation95%	GeneralComment
Air emission	662	Location				
	493	InfrastructureProcess				
	403	Unit				
	Heat, waste	MJ	1.91E+01			Uncertainty for LCI results cannot be determined
	Particulates, > 10 um	kg	1.43E-04			Uncertainty for LCI results cannot be determined
	Particulates, > 2.5 um, and < 10um	kg	1.93E-04			Uncertainty for LCI results cannot be determined
	Particulates, < 2.5 um	kg	1.12E-04			Uncertainty for LCI results cannot be determined
	Carbon monoxide, fossil	kg	2.16E-03			Uncertainty for LCI results cannot be determined
	Carbon monoxide, biogenic	kg	4.97E-06			Uncertainty for LCI results cannot be determined
	Carbon dioxide, fossil	kg	1.30E+00			Uncertainty for LCI results cannot be determined
	Carbon dioxide, biogenic	kg	3.01E-03			Uncertainty for LCI results cannot be determined
	Sulfur dioxide	kg	2.78E-03			Uncertainty for LCI results cannot be determined
	Hydrogen sulfide	kg	1.12E-08			Uncertainty for LCI results cannot be determined
	Nitrogen oxides	kg	2.35E-03			Uncertainty for LCI results cannot be determined
	Ammonia	kg	1.23E-10			Uncertainty for LCI results cannot be determined
	Chlorine	kg	6.33E-11			Uncertainty for LCI results cannot be determined
	Hydrogen chloride	kg	2.86E-05			Uncertainty for LCI results cannot be determined
	Fluorine	kg	2.23E-11			Uncertainty for LCI results cannot be determined
	Hydrogen fluoride	kg	1.07E-06			Uncertainty for LCI results cannot be determined
	NMVOC, non-methane volatile organic compounds, unspecified origin	kg	1.95E-03			Uncertainty for LCI results cannot be determined
	Aldehydes, unspecified	kg	6.11E-16			Uncertainty for LCI results cannot be determined
	Lead	kg	5.11E-10			Uncertainty for LCI results cannot be determined
	Mercury	kg	1.09E-09			Uncertainty for LCI results cannot be determined
	Sulfate	kg	3.11E-15			Uncertainty for LCI results cannot be determined
	Dinitrogen monoxide	kg	7.50E-11			Uncertainty for LCI results cannot be determined
	Hydrogen	kg	2.96E-05			Uncertainty for LCI results cannot be determined
	Ethane, 1,2-dichloro-	kg	1.02E-11			Uncertainty for LCI results cannot be determined
	Ethene, chloro-	kg	2.08E-10			Uncertainty for LCI results cannot be determined
	Halogenated hydrocarbons, chlorinated	kg	4.21E-09			Uncertainty for LCI results cannot be determined
	Cyanide	kg	2.08E-18			Uncertainty for LCI results cannot be determined
	Methane, fossil	kg	1.29E-02			Uncertainty for LCI results cannot be determined
	Methane, biogenic	kg	2.97E-05			Uncertainty for LCI results cannot be determined
	Hydrocarbons, aromatic	kg	2.89E-05			Uncertainty for LCI results cannot be determined
	Hydrocarbons, aliphatic, alkanes, cyclic	kg	1.12E-05			Uncertainty for LCI results cannot be determined
	Carbon disulfide	kg	6.43E-11			Uncertainty for LCI results cannot be determined
	Methane, dichloro-, HCC-30	kg	1.81E-13			Uncertainty for LCI results cannot be determined
	Copper	kg	1.79E-11			Uncertainty for LCI results cannot be determined
	Arsenic	kg	6.30E-11			Uncertainty for LCI results cannot be determined
	Cadmium	kg	1.41E-11			Uncertainty for LCI results cannot be determined
	Silver	kg	5.89E-14			Uncertainty for LCI results cannot be determined
	Zinc	kg	4.93E-11			Uncertainty for LCI results cannot be determined
	Chromium	kg	6.15E-06			Uncertainty for LCI results cannot be determined
	Selenium	kg	2.04E-15			Uncertainty for LCI results cannot be determined
	Nickel	kg	1.12E-05			Uncertainty for LCI results cannot be determined
	Antimony	kg	1.77E-15			Uncertainty for LCI results cannot be determined
	Ethene	kg	2.86E-06			Uncertainty for LCI results cannot be determined
	Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin	kg	1.15E-31			Uncertainty for LCI results cannot be determined
	Benzene	kg	3.92E-06			Uncertainty for LCI results cannot be determined
	Toluene	kg	2.16E-06			Uncertainty for LCI results cannot be determined
	Xylene	kg	1.40E-06			Uncertainty for LCI results cannot be determined
	Benzene, ethyl-	kg	8.40E-07			Uncertainty for LCI results cannot be determined
	Styrene	kg	5.65E-10			Uncertainty for LCI results cannot be determined
	Propene	kg	2.12E-06			Uncertainty for LCI results cannot be determined

Tab. 96.7 Emission to water data for xylene production in Europe (colours according to explanations in Hischier (2007))

Explanation	401	Name	Unit	xylene, at plant	RER 0 kg	uncertaintyType	standardDeviation95%	GeneralComment	
								Location	standardDeviation95%
								InfrastructureProcess Unit	standardDeviation95%
Water emission	662 493 403	COD, Chemical Oxygen Demand	kg	2.31E-04				Uncertainty for LCI results cannot be determined	
		BOD ₅ , Biological Oxygen Demand	kg	5.17E-05				Uncertainty for LCI results cannot be determined	
		Lead	kg	2.41E-10				Uncertainty for LCI results cannot be determined	
		Iron, ion	kg	1.42E-08				Uncertainty for LCI results cannot be determined	
		Sodium, ion	kg	1.20E-04				Uncertainty for LCI results cannot be determined	
		Acidity, unspecified	kg	1.64E-06				Uncertainty for LCI results cannot be determined	
		Nitrate	kg	4.34E-06				Uncertainty for LCI results cannot be determined	
		Mercury	kg	1.41E-10				Uncertainty for LCI results cannot be determined	
		Ammonium, ion	kg	1.89E-06				Uncertainty for LCI results cannot be determined	
		Chloride	kg	9.88E-05				Uncertainty for LCI results cannot be determined	
		Cyanide	kg	3.15E-11				Uncertainty for LCI results cannot be determined	
		Fluoride	kg	1.23E-09				Uncertainty for LCI results cannot be determined	
		Sulfide	kg	1.08E-11				Uncertainty for LCI results cannot be determined	
		Hydrocarbons, unspecified	kg	1.70E-05				Uncertainty for LCI results cannot be determined	
		Suspended solids, unspecified	kg	7.94E-05				Uncertainty for LCI results cannot be determined	
		Oils, unspecified	kg	2.97E-05				Uncertainty for LCI results cannot be determined	
		Chlorinated solvents, unspecified	kg	5.59E-09				Uncertainty for LCI results cannot be determined	
		Chlorine	kg	1.28E-09				Uncertainty for LCI results cannot be determined	
		Phenol	kg	6.03E-07				Uncertainty for LCI results cannot be determined	
		Solved solids	kg	2.15E-05				Uncertainty for LCI results cannot be determined	
		Phosphorus	kg	5.50E-08				Uncertainty for LCI results cannot be determined	
		Nitrogen	kg	2.64E-06				Uncertainty for LCI results cannot be determined	
		Sulfate	kg	3.77E-04				Uncertainty for LCI results cannot be determined	
		Ethane, 1,2-dichloro-	kg	2.25E-13				Uncertainty for LCI results cannot be determined	
		Ethene, chloro-	kg	3.85E-12				Uncertainty for LCI results cannot be determined	
		Potassium, ion	kg	1.46E-10				Uncertainty for LCI results cannot be determined	
		Calcium, ion	kg	2.78E-08				Uncertainty for LCI results cannot be determined	
		Magnesium	kg	5.46E-10				Uncertainty for LCI results cannot be determined	
		Chromium, ion	kg	5.68E-12				Uncertainty for LCI results cannot be determined	
		Chlorate	kg	9.77E-08				Uncertainty for LCI results cannot be determined	
		Bromate	kg	6.62E-10				Uncertainty for LCI results cannot be determined	
		TOC, Total Organic Carbon	kg	3.36E-05				Uncertainty for LCI results cannot be determined	
		AOX, Adsorbable Organic Halogen as Cl	kg	6.40E-13				Uncertainty for LCI results cannot be determined	
		Aluminum	kg	1.12E-06				Uncertainty for LCI results cannot be determined	
		Zinc, ion	kg	3.84E-08				Uncertainty for LCI results cannot be determined	
		Copper, ion	kg	1.93E-08				Uncertainty for LCI results cannot be determined	
		Nickel, ion	kg	3.64E-10				Uncertainty for LCI results cannot be determined	
		Carbonate	kg	1.15E-04				Uncertainty for LCI results cannot be determined	
		Arsenic, ion	kg	5.43E-10				Uncertainty for LCI results cannot be determined	
		Cadmium, ion	kg	4.40E-15				Uncertainty for LCI results cannot be determined	
		Manganese	kg	1.73E-14				Uncertainty for LCI results cannot be determined	
		Tin, ion	kg	2.31E-16				Uncertainty for LCI results cannot be determined	
		Strontium	kg	1.02E-11				Uncertainty for LCI results cannot be determined	
		Silicon	kg	1.30E-19				Uncertainty for LCI results cannot be determined	
		Benzene	kg	9.95E-22				Uncertainty for LCI results cannot be determined	
		Molybdenum	kg	-				Uncertainty for LCI results cannot be determined	

96.8 Cumulative results and interpretation

Results of the cumulative inventory for this substance can be downloaded from the database.

96.9 Conclusions

The inventory data used in this process does not give transparency on the processes used and allocations made due to the use of cumulated data. Therefore, many emissions especially soil emissions are not accounted. Because of the cumulated data also no land occupation and land transformation could be included in the dataset. This leads to an incompleteness of the dataset, which has to be considered when using it. Also the uncertainty of the data used could not be determined for those datasets. Nevertheless the data refers on a large share of the European production and should therefore be representative for the production of this chemical.

96.10EcoSpold Meta Information

ReferenceFunction	401	Name	xylene, at plant
Geography	662	Location	RER
ReferenceFunction	493	InfrastructureProcess	0
ReferenceFunction	403	Unit	kg
ReferenceFunction	402	IncludedProcesses	Aggregated data for all processes from raw material extraction until delivery at plant
ReferenceFunction	404	Amount	1
ReferenceFunction	490	LocalName	Xylol, ab Werk
ReferenceFunction	491	Synonyms	
ReferenceFunction	492	GeneralComment	Data are from the Eco-profiles of the European plastics industry (PlasticsEurope). Not included are the values reported for: recyclable wastes, amount of air / N ₂ / O ₂ consumed, unspecified metal emission to air and to water, mercaptan emission to air, unspecified CFC/HCFC emission to air, dioxin to water. The amount of "sulphur (bonded)" is assumed to be included into the amount of raw oil.
ReferenceFunction	502	CASNumber	
TimePeriod	601	StartDate	2001
TimePeriod	602	EndDate	2002
TimePeriod	603	DataValidForEntirePeriod	1
TimePeriod	611	OtherPeriodText	time to which data refer
Geography	663	Text	11 European plants
Technology	692	Text	production by catalytic reforming out of naphtha
Representativeness	722	Percent	
Representativeness	724	ProductionVolume	1.4 Mt in Europe in 2000
Representativeness	725	SamplingProcedure	literature values based on company survey
Representativeness	726	Extrapolations	no extrapolation
Representativeness	727	UncertaintyAdjustments	none

96.11 References

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97 Zirconium oxide production from mineral sands

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Review: Rolf Frischknecht, ESU-services Ltd., Uster

Last changes:

10.12.2007

97.1 Introduction

Zirconium silicate, also called *zircon* (ZrSiO_4), is the main commercial zirconium mineral. A relatively small quantity of zirconium is derived from baddeleyite, a natural form of zirconium oxide (ZrO_2). Zircon is normally produced as a by-product of the mining and processing of heavy-mineral sands containing the titanium minerals ilmenite and rutile. Large heavy mineral deposits are mined in Florida, West Australia, South Africa, India, Russia and Kazakhstan.

The purest zircon is extracted and refined for use in the *zirconium metals*. Less pure deposits are used in the form of stabilized *zirconia* (zirconium dioxide) for refractories and ceramic products.

97.2 Characterisation of material product

The heavy mineral component in mineral sand comprises varying proportions of magnetite, ilmenite, rutile, zircon and silica. The valuable heavy minerals (ilmenite, rutile and zircon) are generally finer grained than either the other heavy minerals or the host sand. Zirconium dioxide (ZrO_2), also known as zirconia, is a powder of white, white-grey or slightly yellow colour. Tab. 97.1 shows the physical properties of zirconia (ZrO_2), zircon (ZrSiO_4), rutile and ilmenite.

Tab. 97.1 Physical properties of zirconia, zircon, rutile and ilmenite

Property	Unit	Zirconia	Zircon	Rutile	Ilmenite
Chemical formula	-	ZrO_2	ZrSiO_4	TiO_2	FeTiO_3
CAS number	-	1312-81-8	14940-68-2	1317-80-2	98072-94-7
Molecular weight	g mol^{-1}	123.22	183.30	79.88	151.73
Specific gravity ¹	kg dm^{-3}	5.89	4.6-4.8	4.0 - 4.3	4.3-4.6
Bulk density ¹	kg dm^{-3}	2.8	2.7-2.95	2.4-2.7	2.4-2.7
Melting point	$^{\circ}\text{C}$	2715	2200	1825	1050

97.3 Reserves and resources of the material

The typical valuable minerals in mineral sands include ilmenite (FeTiO_3), rutile (TiO_2) and zircon (ZrSiO_2). Leucoxene (FeTiO_3 TiO_2) and monazite ($\text{Ce, La, Th, Nd, YPO}_4$) are also recovered in some mines. The size and grade of the mineral sand deposits vary considerably. Shoreline deposits are typically 100 or 200 m wide, 2 to 20 km long and 5 to 20 m thick. Heavy mineral grades vary from several percent to 90 percent. Most mines no longer process monazite due to the decreased world demand for thorium-bearing rare earth concentrates and the increased cost of thorium disposal.

Zircon is the primary source of hafnium. Zircon contains zirconium and hafnium at a ratio of about 50 to 1.

In 2005, zircon was mined at many locations worldwide, primarily Australia, South Africa, and the United States. Baddeleyite is derived from a single source in Kovdor, Russia. Western Australia produces around 445,000 tonnes p.a. of zirconium mineral, representing more than one-third of world production. There are four producers of titanium mineral. An Australian publication estimated that world zirconium production increased from 1.15 Mt in 2004 to 1.18 million metric tons (Mt) in 2005 (Mineral Sands Report, 2006). Australia and South Africa supplied about 69% of all production out-

side the United States. World reserves of zircon are estimated to be 38 Mt of zirconium oxide, 50 Mt of rutile and 600 Mt of ilmenite (Gambogi 2006b, Gambogi 2006c).

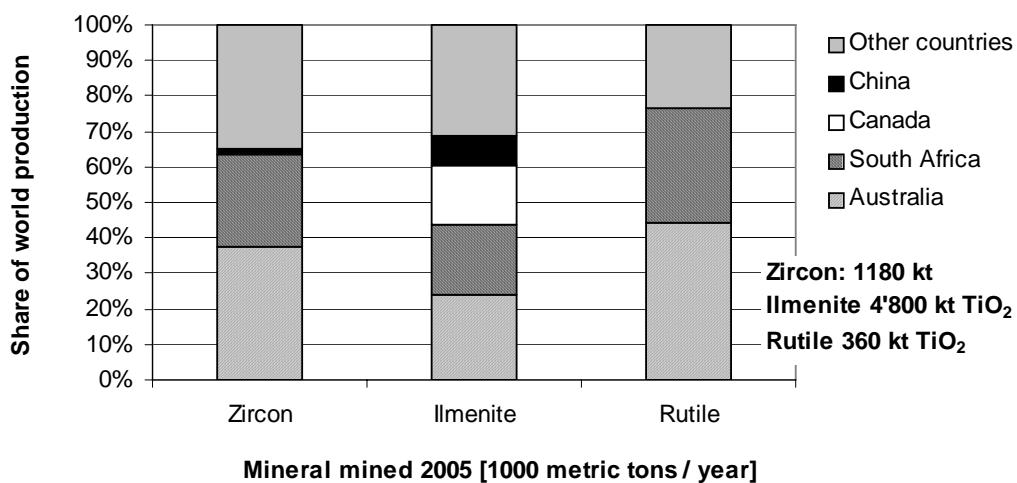


Fig. 97.1 Distribution of world production of zircon, rutile and ilmenite (Gambogi, 2006a, Gambogi, 2006b)

97.4 Use / application of the product

In 2005, global demand for zirconium minerals continued to exceed supply. With a share of 35%, Europe has long been the principle consuming region. Due to its fast growing output of tiles (more than 20% in 2002) China is becoming a leading zirconium consumer. This development has significantly influenced the price and availability of zirconium minerals (Gambogi, 2006a).

World demand for ilmenite and rutile is driven by the demand for titanium oxide pigment, which makes up 95 per cent of its use. Rutile is also used as a source of titanium metal. Zircon is a zirconium silicate used in the ceramic, refractory and foundry industries. Approximately 95% of zirconium is sold as zircon, zirconium oxide or other zirconium chemicals. The remainder is consumed as zirconium metal and zirconium-containing alloys.

97.5 System characterisation

The sand and gravel that contain zircon mixed with silicate, ilmenite, and rutile are typically collected by wet or dry mining techniques. The mining operations use floating dredges or self-elevating scrapers to cut the ore. The material is purified by means of spiral concentrators, which separate it on the basis of density. The ilmenite and rutile are then removed by magnetic and electrostatic separators and sold as bulk products, mainly for titanium dioxide production. The purest concentrates of zircon are shipped to end-product manufacturers to be used in metal production, while less pure concentrates are used for refractories.

The production of zirconium oxide (zirconia) from zircon ($ZrSiO_4$) requires the use of high temperatures and aggressive chemicals to decompose the zircon. Caustic fusion is the usual process used to decompose the zircon (Nielsen & Chang, 2005). It is described in this inventory. Other processes used to decompose zircon are fluidized-bed carbochlorination, thermal dissociation of zircon in an arc plasma or direct electric-arc smelting of zircon to make fused zirconia.

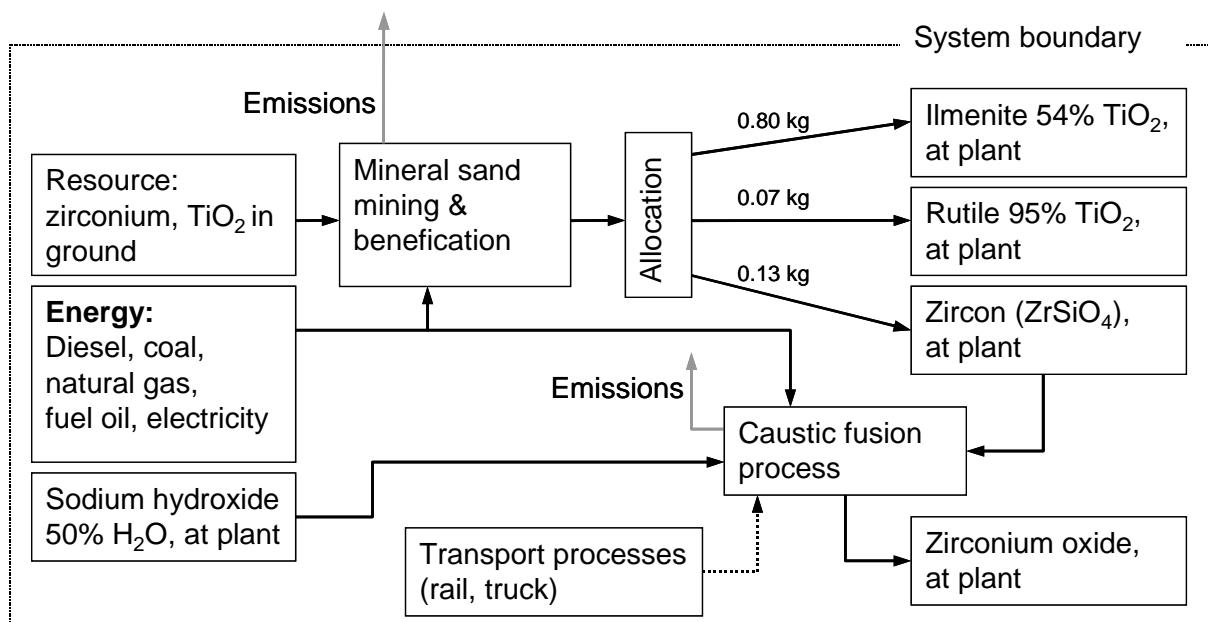


Fig. 97.2 System outline for zircon and zircon oxide production from mineral sands

Because zircon, ilmenite and rutile products are mined and beneficiated together, the environmental burdens of the beneficiation process are allocated to these three products:

- zircon, 50% zirconium, at plant
- ilmenite, 54% titanium dioxide, at plant
- rutile, 95% titanium dioxide, at plant

Zirconium oxide is derived from the zircon product by caustic fusion (zirconium oxide, at plant).

97.6 Zircon production from mineral sands

97.6.1 Process

This inventory describes the mining process for ilmenite, rutile and zircon from mineral sands. It is based on the usual mining and beneficiation process used in Australian operations (Iluka, 2005). Wet or dry mining techniques are used. Wet mining operations use a floating dredge to cut the ore under the surface of a pond and then pump the ore slurry to a wet concentrator. In dry mining techniques, the ore is mined with front-end loaders and self-elevating scrapers and deposited into a hopper.

The crude ore is screened and scrubbed in order to remove oversize material,¹⁷ which is returned to the mining pit. The heavy mineral is separated from the sand through gravity separation. Sand residue from the concentration process is pumped back to the mining pit. The sand is re-contoured there before the overburden and topsoil are replaced.

After wet processing, the heavy mineral concentrate goes through dry processing stages to separate the valuable minerals. Dry mill processing uses screening, magnetic, electrostatic and gravity separation circuits. The ilmenite, rutile and zircon minerals are separated in this process step.

A part of the ilmenite produced is often upgraded to synthetic rutile (SR). In this process, the ilmenite is treated in large rotary kilns in order to remove the non-titanium components. Synthetic rutile has a

¹⁷ Oversize material can consist of: rocks, clay, organic matter, other debris

titanium dioxide (TiO_2) content of 88 to 95 per cent and is therefore similar to the naturally formed rutile mineral. This upgrading process of ilmenite is not included in this inventory.

A simplified process flowchart of zircon production from mineral sands is shown in Fig. 97.3.

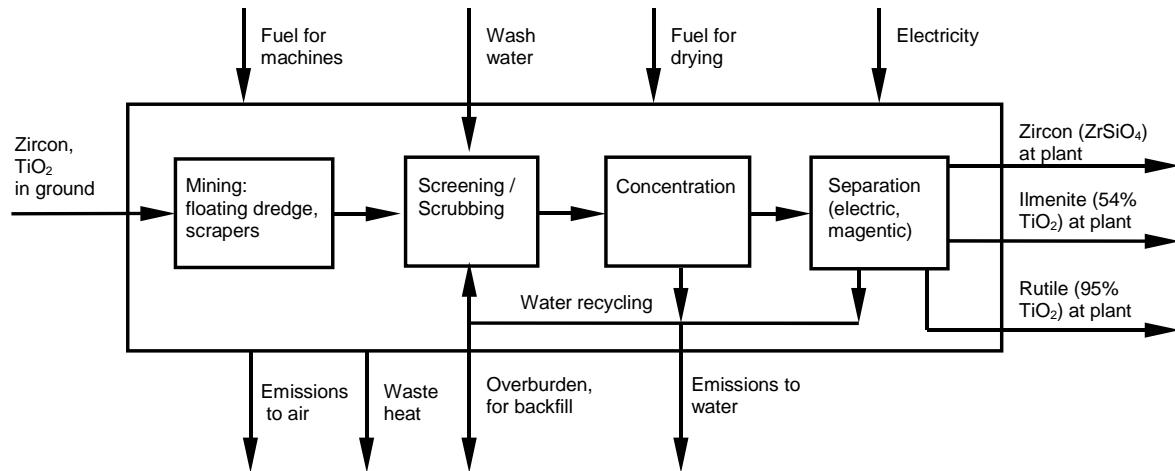


Fig. 97.3 Simplified process flowchart of zircon production from mineral sands

97.6.2 Resources

The heavy mineral concentration in the mined sands can vary considerably. According to Taylor et al. (2003), the variation may range between 2 and 25 percent in one deposit. According to Nielsen & Chang (2005), the heavy mineral concentration ranges from 4 to 7 percent of the ore. According to Cable Sands (2000), an average of 11.4 kg of ore body is removed for each kg of heavy mineral concentrate, which equals a concentration of 8.8 percent. This inventory is based on a concentration of 6 percent.

In the production process investigated here, 1 kg of heavy mineral concentrate consists (average of five different mine sites) of 0.8 kg ilmenite, 0.07 kg rutile and 0.13 kg zircon ($ZrSiO_4$). From the concentration and beneficiation process, 0.36 kg tailings (mainly lower specific gravity material such as quartz and silica as well as unrecovered minerals) are deposited, with the oversize material in the mining site (Iluka 2001, Iluka 2002). A yield of 93 to 97 percent is given for the concentration and beneficiation process (Taylor et al., 2003). A yield of 95 percent is used here.

In order to produce 1 kg of heavy mineral concentrate containing 0.8 kg ilmenite, 0.07 kg rutile and 0.13 kg zircon, the following ground resources are needed:

- zirconium, 50% in zircon, 0.39% in crude ore, in ground: 68 g
- TiO_2 , 54% in ilmenite, 2.6% in crude ore, in ground: 455 g
- TiO_2 , 95% in rutile, 0.40% in crude ore, in ground: 70 g

The overburden, topsoil and waste rock are neglected as a resource because they are filled back into the mine and used for reclamation. Monazite (~0.1 wt. percent in the ore) is not considered as a resource either. In most cases, it is not recovered for economical reasons, and is therefore also filled back into the mine together with the tailings.

97.6.3 Energy use and auxiliaries

Process energy, mining and beneficiation

The energy requirement for mining and beneficiation varies from 1.3 to 4.5 MJ per kg of mineral product. This value does not include synthetic rutile production from ilmenite. An average energy requirement of 3.3 MJ per kg of mineral product is calculated from the data of five different mining sites (Iluka 2001, Iluka 2002). The following shares of individual energy carriers are calculated from the average energy mix of total production: 1.2 MJ/kg coal, 0.52 MJ/kg diesel, 0.36 MJ/kg natural gas, 0.12 MJ/kg fuel oil and 0.305 kWh/kg electricity.

In order to include all important energy emissions, the energy requirement is linked to the corresponding furnace or operation processes (see Tab. 97.3)

Treatment chemicals, mining and beneficiation

No information is available on the treatment chemicals, e.g. the flocculant used for the concentration process. The concentration mainly uses physical, magnetic and electrical separation processes. The use of chemicals is therefore assumed to be low and is neglected.

Water resources

The water used in the process is recycled into a clean water dam from which the process water is drawn. The use of fresh water may consequently be very low. Depending on the climate (evaporation) and the mining process used, the fresh water consumption ranges from 4.6 to 116 litres per kg of mineral product. The average from five different mining sites is 17.6 litres per kg of mineral product (Iluka 2001, Iluka 2002). It is assumed that this water is pumped from a well.

97.6.4 Emissions

Emissions to air

CO₂, CO, SO₂, NO_x and other emissions caused by the burning of fuel are included in the linked energy processes.

A constant challenge for mineral sand mining is the dust produced by the mining operations. According to Illuka (2001), it is estimated that 478 tonnes of particulates are emitted from the stacks on processing sites. This equals 0.25 g particulates per kg of mineral product. Depending on the operation (climate, dry/wet processing), this value ranges from 0.02 to 0.77 g per kg of mineral product. The particle size distribution of the emissions from material handling is estimated on the basis of the data presented in CEIDARS (2000) and EPA (1998a) for rock screening, rock handling and unpaved road transport. The particle size distribution ranges from 7% to 17% PM 2.5 and from 25% to 59% PM 10. The following distribution is used for the particle emissions: 58% for > 10 µm, 30% for 2.5-10 µm and 12% for < 2.5 µm particle size.

About 0.1% of the processed ore material is monazite (Iluka 2001), which has higher radioactivity due to its thorium and uranium content. According to EPA (1998b), the activity of monazite ranges from 22.2 to 111 kBq/kg (average: 66.6 kBq/kg) for uranium 238, from 107 to 2,960 kBq/kg (average: 144 kBq/kg) for thorium 232 and an average of 22.9 kBq/kg for radium 226. Assuming that 0.25 g per kg product (0.1 wt-%) is also monazite in the dust emissions, the following radioactive emissions to air are calculated per kg of product: 0.0167 Bq for uranium 238, 0.036 Bq for thorium 232 and 0.0573 Bq for radium 226.

Emissions to water

The average from five different mining sites is 2.3 litres of waste water per kg of mineral product (Iluka 2001, Iluka 2002). Depending on the process used (dry/wet processing), this value ranges from 0 to 5.6 litres per kg of mineral product. No information is available on the composition of this waste water. According to the emission limits set for mining mineral sands by EPA (2004), the pollutants are mainly suspended solids and iron. An emission level of 20 mg of suspended solids and 1 mg of iron per litre of waste water is used for this inventory. This equals the limit for average daily values for 30 consecutive days according to EPA (2004).

Wastes

No relevant waste is produced in the mining process. The overburden is used for the re-cultivation of the mine and is not treated as waste. Due to finer fractions and possibly increased weathering, however, greater amounts of components of the backfilled material may get into the ground water compared to the situation prevailing before the mining activity. Due to lack of data no such long term emissions are included.

Monazite is a fairly common minor mineral present in most mineral-sand deposits. Due to its density and physical properties, it concentrates in the dry mill, and especially in the zircon streams. Apart from the dust emissions, no special waste treatment for the monazite residues are included.

97.6.5 Land use

According to (Cable Sands 2000, Iluka 2001, Iluka 2002), the land use for a mineral sand mine averages 2.7 m^2 per metric ton of beneficiated heavy mineral product (zircon, ilmenite and rutile). The land use ranges from 1.4 up to 14 m^2 per metric ton of mineral product. A transformation to a mineral extraction site of $2.7 * 10^{-3} \text{ m}^2$ per kg of mineral product is used here. According to Cable Sands (2000), about 40% of the mined area in a typical mining area was previously woodland (open forest). The rest (mainly pasture) is accounted as pasture.

For the re-cultivation of the mine site, a similar land transformation as that for bauxite mines is assumed (55% farm land, 22% extensive farm land, 22% forest, 1% industrial area). For the re-cultivation, the process “recultivation, bauxite mine” is used as an approximation ($2.7 * 10^{-3} \text{ m}^2$ per kg of mineral product).

During mining operation, an occupation of a “mineral extraction site” with an average operating time of 10 years is assumed (Cable Sands, 2000). The reclamation is included in the 10-year operating time due to the continuous reclamation of mined land sectors. This leads to an occupation of $27 * 10^{-3} \text{ m}^2$ a per kg of mineral product.

97.6.6 Infrastructure

No specific data are available for the mining infrastructure. The infrastructure of the mine is approximated with the process “bauxite mine” which characterises a mine with an output of $1 * 10^6$ tons of bauxite per year over 20 years. Due to the lower ore concentration (6% instead of 48% for bauxite mining), the infrastructure requirement is assumed to be eight times higher. This assumption is based on the much greater material throughput for zircon mining (larger machines for screening and separation). This leads to an infrastructure requirement of $0.4 * 10^{-9}$ “bauxite mine” units per kg of mineral product.

97.6.7 Allocation of zircon, ilmenite and rutile products

Zircon, ilmenite and rutile are processed as saleable products from the mining and beneficiation of mineral sands. From the production process described, 1 kg of heavy mineral concentrate consists on average of 0.8 kg of ilmenite, 0.07 kg of rutile and 0.13 kg of zircon (ZrSiO_4). The energy input, emissions and infrastructure expenditures are allocated to these products.

Various concepts may be used for the allocation. The revenue is used as an allocation scheme. In such a case, the product with the higher specific value is assigned a higher environmental burden than the product with a low price. The allocation factors are determined according to the average bulk prices for rutile, ilmenite and zircon of between 2000 and 2005 (Mineral Sands Report 2001, Gambogi 2006b, Gambogi 2006c). Tab. 97.2 summarises the resulting allocation factors and underlying assumptions.

Tab. 97.2 Allocation factors applied to zircon production from mineral sands

	Amount [kg]	Value [\$/ton] *)	Allocation factor
Zircon, 50% zirconium, at plant	0.13	437	36 %
Ilmenite, 54% titanium dioxide, at plant	0.80	87	44 %
Rutile, 95% titanium dioxide, at plant	0.07	459	20 %

*) Based on average bulk prices 2000-2005; Australian export, FOB (US-\$)

97.6.8 Data quality considerations

Tab. 97.3 shows the multi-output process raw data and data-quality indicators of the inventory of zircon production from mineral sands.

A simplified approach with a pedigree matrix is used to calculate the standard deviation. However, the basic uncertainty has been adjusted when necessary to represent the ranges of the data obtained from a study of the literature. The inventory is based on various mining sites which represent the following share of worldwide production: 27% for zircon, 24% for ilmenite and 40% for rutile. The highest uncertainties are for particle emissions, fresh water use and land use because the data are derived from different mining processes. The emissions to water and the infrastructure also have a high uncertainty because of the lack of data.

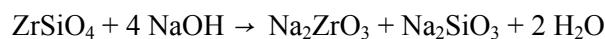
Tab. 97.3 Multi-output process raw data of zircon production from mineral sands

	Name	Location	InfrastructureProcess	Unit	zircon production from mineral sands	UncertaintyType	StandardDeviation95%	GeneralComment	zircon, 50% zirconium, at plant			ilmenite, 54% titanium dioxide, at plant			rutile, 95% titanium dioxide, at plant		
									AU	0	kg	AU	0	kg	AU	0	kg
technosphere	allocated zircon, 50% zirconium, at plant		AU	0	kg	1.30E-1			100	0	0	0	0	0	0	0	0
	allocated ilmenite, 54% titanium dioxide, at plant		AU	0	kg	8.00E-1			0	100	0	0	0	0	0	0	0
	allocated rutile, 95% titanium dioxide, at plant		AU	0	kg	7.00E-2			0	0	0	0	0	0	0	0	100
	diesel, burned in building machine	GLO	0	MJ	5.20E-1	1	1.10	(2,2,2,2,1,3); average from 5 mines	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	hard coal, burned in industrial furnace 1-10MW	RER	0	MJ	1.20E+0	1	1.10	(2,2,2,2,1,3); average from 5 mines	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	natural gas, burned in industrial furnace >100kW	RER	0	MJ	3.60E-1	1	1.10	(2,2,2,2,1,3); average from 5 mines	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	heavy fuel oil, burned in industrial furnace 1MW, non-modulating	RER	0	MJ	1.20E-1	1	1.10	(2,2,2,2,1,3); average from 5 mines	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	electricity, medium voltage, production UCTE, at grid	UCTE	0	kWh	3.05E-1	1	1.10	(2,2,2,2,1,3); average from 5 mines	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
resource, land	mine, bauxite recultivation, bauxite mine	GLO	1	unit	4.00E-10	1	3.38	(4,5,3,3,4,5); estimated	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Transformation, from forest	-	-	m2	1.08E-3	1	2.11	(2,4,2,2,3,5); area as average from 5 mines, other data from one mine	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Transformation, from pasture and meadow	-	-	m2	1.62E-3	1	1.40	(2,4,2,2,3,5); area as average from 5 mines, other data from one mine	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Transformation, to mineral extraction site	-	-	m2	2.70E-3	1	2.11	(2,4,2,2,3,5); area as average from 5 mines, other data from one mine	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
resource, in water	Occupation, mineral extraction site	-	-	m2a	2.70E-2	1	1.64	(2,4,2,2,3,5); area as average from 5 mines, other data from one mine	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Water, well, in ground	-	-	m3	1.76E-2	1	1.10	(2,2,2,2,1,3); average from 5 mines	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
resource, in ground	TiO2, 54% in ilmenite, 2.6% in crude ore, in ground	-	-	kg	4.55E-1	1	1.27	(3,3,3,2,1,5); uncertainty of ore composition	-	100.0	-	-	-	-	-	-	-
	TiO2, 95% in rutile, 0.40% in crude ore, in ground	-	-	kg	7.00E-2	1	1.27	(3,3,3,2,1,5); uncertainty of ore composition	-	-	-	-	-	-	-	-	100.0
	Zirconium, 50% in zircon, 0.39% in crude ore, in ground	-	-	kg	6.80E-2	1	1.27	(3,3,3,2,1,5); uncertainty of ore composition	100.0	-	-	-	-	-	-	-	-
emission air, low population	Particulates, > 10 um	-	-	kg	1.45E-4	1	2.33	(4,3,2,2,5,5); large variability from mine to mine	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Particulates, > 2.5 um, and < 10um	-	-	kg	7.50E-5	1	2.76	(4,3,2,2,5,5); large variability from mine to mine	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Particulates, < 2.5 um	-	-	kg	3.00E-5	1	3.76	(4,3,2,2,5,5); large variability from mine to mine	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Uranium-238	-	-	kBq	1.67E-5	1	3.76	(4,3,2,2,5,5); estimated from dust emissions	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Thorium-232	-	-	kBq	3.60E-5	1	3.76	(4,3,2,2,5,5); estimated from dust emissions	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Radium-226	-	-	kBq	5.73E-5	1	3.76	(4,3,2,2,5,5); estimated from dust emissions	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Heat, waste	-	-	MJ	1.10E+0	1	1.10	(2,2,2,2,1,3); calculated from electricity input	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
emission water, river	Suspended solids, unspecified	-	-	kg	4.60E-5	1	2.37	(4,5,2,2,5,5); estimation, high uncertainty	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0
	Iron, ion	-	-	kg	2.30E-6	1	5.93	(4,5,2,2,5,5); estimation, high uncertainty	36.0	44.0	20.0	36.0	44.0	20.0	36.0	44.0	20.0

97.7 Zirconium oxide, at plant

97.7.1 Process

In the caustic fusion process, zircon ore is fused with a slight excess of sodium hydroxide at 650 °C. Caustic fusion is the standard process used to decompose zircon (Nielsen & Chang, 2005).



The product of the fusion is slurried in water to dissolve and remove the silicon as sodium silicate. The insoluble hydrous zirconia is recovered by filtration and can be fired to zirconium oxide at a temperature of 800 to 1100°C (Nielsen & Chang, 2005). No environmental burdens of the process are allocated to the sodium silicate by-product because this is of lesser value and is often not saleable either.

97.7.2 Resources

For the production of 1 kg of zirconium oxide, 1.57 kg of zircon (ZrSiO_4) is needed assuming a process yield of 95% for zirconium.

97.7.3 Energy use and auxiliaries

No process-specific information is available on energy and auxiliary material use. The energy and auxiliary material requirement of the caustic fusion process is approximated with data from the production of hydrothermal sodium silicate (Zah & Hischier, 2007). The calcination of the hydrous zirconia to zirconium oxide is approximated with data from the production of aluminium oxide from aluminium hydroxide (Classen et al. (2007)). The amount of sodium hydroxide (NaOH) needed is calculated from the stoichiometric requirement, including an excess of 10% NaOH.

Tab. 97.4 Energy use and auxiliaries for zirconium oxide production from zircon with caustic fusion

	Unit	Stoichiometric calculation	Hydrothermal sodium silicate	Aluminium oxide from aluminium hydroxide	Used in this inventory
Zircon (ZrSiO_4)	kg	1.49	-	-	1.57 *)
Sodium hydroxide	kg	1.30	0.435	-	1.44 *)
Organic chemicals	kg	-	0.00146	-	0.00146
Water (process, cooling)	m3	-	0.00162	-	0.00162
Electricity	kWh	-	0.0308	0.0105	0.04
Heat, hard coal	MJ	-	0.0541	-	0.0541
Heat, fuel oil	MJ	-	0.00857	1.94	2
Heat, natural gas	MJ	-	0.732	0.507	1.2
Steam	kg	-	0.297	-	0.3
Sodium silicate **)	kg	1.00	1.00	-	(1.00) **)
Zirconium oxide (ZrO_2)	kg	1.00	-	(1.00 kg Al_2O_3)	1.00

*) 95% yield for zircon (ZrSiO_4); 10% excess of sodium hydroxide assumed

**) By-product; no environmental burdens allocated due to low value

97.7.4 Emissions

Emissions to air

Emissions to air are included in the unit processes for energy use. No further process-related emissions are included.

Emissions to water, wastes

No process-specific information is available on emissions to water and waste materials. The water emissions and wastes of the caustic fusion process are approximated with data from the production of hydrothermal sodium silicate (Zah & Hischier, 2007).

97.7.5 Transport processes

The transport of zircon and the auxiliary materials to the plant is considered with the standard distances for base chemicals (100 km road and 600 km rail) because no specific transport distances are available. Based on this assumption, 0.45 tkm road transport and 2.67 tkm rail transport are included in the inventory.

97.7.6 Infrastructure

No specific data are available for the infrastructure of the production process. The infrastructure of the process is approximated, analogously to the production of hydrothermal sodium silicate, with the process “chemical plant, organics”. In order to cover both process steps, an infrastructure requirement of $8 * 10^{-10}$ units “chemical plant, organics” per kg zirconium oxide is used.

97.7.7 Data quality considerations

Tab. 97.5 shows the unit process raw data and data-quality indicators of the inventory of zirconium oxide, at plant.

A simplified approach with a pedigree matrix is used to calculate the standard deviation. However, the basic uncertainty is adjusted to represent the ranges of the data obtained from a study of the literature or similar processes. As the data are approximated with information from sodium silicate and aluminium oxide production, the uncertainty in the inventory is high. The highest uncertainties exist for emissions and wastes. Because of missing data, these values are based on approximations from sodium silicate production. Further uncertainty is due to the possible lack of auxiliary materials and further emissions or wastes. Large uncertainties also exist for the data for transport distances and the infrastructure.

Tab. 97.5 Unit process raw data of zirconium oxide, at plant

product	Name	Location	InfrastructureProcess	Unit	zirconium oxide, at plant	UncertaintyType	StandardDeviation95%	GeneralComment
	Location	InfrastructureProcess	Unit	AU 0 kg			%	
technosphere	zirconium oxide, at plant	AU 0 kg		1				
	zircon, 50% zirconium, at plant	AU 0 kg		1.57E+0	1	1.13	(2,nA,nA,3,1,4); input calculated from stoichiometry	
	sodium hydroxide, 50% in H ₂ O, production mix, at plant	RER 0 kg		1.44E+0	1	1.13	(2,nA,nA,3,1,4); data from hydrothermal sodium silicate	
	chemicals organic, at plant	GLO 0 kg		1.46E-3	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	electricity, medium voltage, production UCTE, at grid	UCTE 0 kWh		4.13E-2	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	heat, light fuel oil, at industrial furnace 1MW	RER 0 MJ		2.00E+0	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	heat, natural gas, at industrial furnace >100kW	RER 0 MJ		1.20E+0	1	1.65	(4,5,3,3,4,4); data from sodium silicate and aluminium hydroxide production	
	heat, at hard coal industrial furnace 1-10MW	RER 0 MJ		5.41E-2	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	steam, for chemical processes, at plant	RER 0 kg		3.00E-1	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	chemical plant, organics	RER 1 unit		8.00E-10	1	3.79	(4,5,3,3,5,4); estimation	
	transport, freight, rail	RER 0 tkm		2.67E+0	1	2.09	(4,5,nA,nA,nA,nA); standard distances used	
	transport, lorry >16t, fleet average	RER 0 tkm		4.50E-1	1	2.09	(4,5,nA,nA,nA,nA); standard distances used	
	disposal, residue from cooling tower, 30% water, to sanitary landfill	CH 0 kg		2.50E-3	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	disposal, inert waste, 5% water, to inert material landfill	CH 0 kg		1.81E-2	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	disposal, average incineration residue, 0% water, to residual material landfill	CH 0 kg		4.16E-5	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
resource, in water	Water, cooling, unspecified natural origin	- - m3		2.08E-5	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	Water, unspecified natural origin	- - m3		1.60E-3	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
emission air, high population density	Heat, waste	- - MJ		1.02E+0	1	1.65	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
emission water, river	COD, Chemical Oxygen Demand	- - kg		1.31E-5	1	1.90	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	Suspended solids, unspecified	- - kg		1.27E-3	1	1.90	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	Nitrate	- - kg		2.91E-7	1	1.90	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	Phosphate	- - kg		2.08E-8	1	1.90	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	Chloride	- - kg		9.78E-5	1	3.34	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	Iron, ion	- - kg		8.32E-8	1	5.39	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	
	Silicon	- - kg		3.41E-3	1	5.39	(4,5,3,3,4,4); data from hydrothermal sodium silicate production used	

97.8 Cumulative results and interpretation

97.8.1 Introduction

Selected LCI results and values for the cumulative energy requirement are presented and discussed in this section. Please note that only a small part of the 1500 elementary flows is presented here. The selection of the elementary flows shown in the tables is not based on their environmental relevance. Rather, it allows the contributions of the different life cycle phases or specific inputs from the technosphere to the selected elementary flows to be illustrated. Please refer to the *ecoinvent* database for the complete LCIs.

The selection shown is unsuitable for a life-cycle assessment of the analysed processes and products. Please download data from the database for your own calculations, not least because of possible minor deviations between the presented results and the database due to corrections and changes made in the background data used as inputs to the relevant dataset.

The *ecoinvent* database also contains the results of life-cycle impact assessments. Assumptions and interpretations are necessary to match current LCIA methods to the *ecoinvent* inventory results. They are described in Frischknecht et al. (2007). You are strongly advised to read the respective sections of the implementation report before applying the LCIA results.

Multi-output process “zircon production from mineral sands”

The major part of the carbon dioxide (91%), NMVOC (71%), nitrogen oxide emissions (75%) and the cumulative energy demand (fossil: 90%, nuclear: 99%) are caused by energy and fuel used for the mining and processing of the mineral. The direct dust emissions of the mine operation cause 61% of the total particle emissions but only 16% of the emissions of particulate < 2.5µm. For particulate < 2.5µm the energy processes used for mining (diesel in building machines) and processing (furnaces and electricity) are dominating with 65% of the total emissions. The land use for mining is with 78% of the total land use dominating.

Tab. 97.6 shows selected LCI results and cumulative energy demands for the multi-output process “zircon production from mineral sands”. The results for the three products (ilmenite, rutile and zircon) presented in Tab. 97.6 depend significantly on the chosen allocation method.

Process “zirconium oxide, at plant”

The major part of the carbon dioxide (83%), NMVOC (78%), nitrogen oxide emissions (85%) and the cumulative energy demand (fossil: 84%, nuclear: 93%) are caused by the zircon raw material and the sodium hydroxide used for the caustic fusion process. The major part of the land use (61%) origin from the mining of the zircon raw material.

Tab. 97.6 shows selected LCI results and cumulative energy demands for the process “zirconium oxide, at plant”

Tab. 97.6 Selected LCI results and the cumulative energy demand for zirconium oxide production from mineral sands

Ecocat	Ecosubcat	Name	Name	ilmenite, 54% titanium dioxide, at plant	rutile, 95% titanium dioxide, at plant	zircon, 50% zirconium, at plant	zirconium oxide, at plant
			Location Unit	AU kg	AU kg	AU kg	AU kg
cumulative energy demand	fossil	non-renewable energy resources, fossil	MJ-Eq	2.73E+00	1.42E+01	1.37E+01	5.11E+01
	nuclear	non-renewable energy resources, nuclear	MJ-Eq	7.52E-01	3.91E+00	3.79E+00	1.90E+01
	primary forest	non-renewable energy resources, primary forest	MJ-Eq	1.67E-06	8.69E-06	8.43E-06	3.89E-05
	water	renewable energy resources, water	MJ-Eq	8.57E-02	4.45E-01	4.31E-01	2.27E+00
	biomass	renewable energy resources, biomass	MJ-Eq	3.02E-02	1.57E-01	1.52E-01	8.70E-01
	wind	renewable energy resources, kinetic (in wind), converted	MJ-Eq	1.39E-02	7.23E-02	7.00E-02	3.49E-01
	geothermal	renewable energy resources, geothermal, converted	MJ-Eq	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	solar	renewable energy resources, solar, converted	MJ-Eq	1.99E-04	1.03E-03	1.00E-03	5.00E-03
selected LCI results	resource	land occupation	m2a	1.90E-02	9.87E-02	9.57E-02	2.45E-01
	air	CO2, fossil	kg	2.11E-01	1.09E+00	1.06E+00	3.84E+00
	air	NMVOC	kg	1.15E-04	5.97E-04	5.79E-04	1.69E-03
	air	nitrogen oxides	kg	8.47E-04	4.40E-03	4.27E-03	1.13E-02
	air	sulphur dioxide	kg	7.44E-04	3.87E-03	3.75E-03	1.25E-02
	air	particulates, <2.5 um	kg	1.03E-04	5.37E-04	5.21E-04	1.42E-03
	water	BOD	kg	2.50E-04	1.30E-03	1.26E-03	4.41E-03
	soil	cadmium	kg	4.10E-11	2.13E-10	2.06E-10	2.49E-09

97.9 Conclusions

Zircon, ilmenite and rutile are usually processed together from mineral sands. The revenue is used as an allocation scheme for the production process. This assumption influences significantly the result for the three products.

For the production of zirconium oxide various process routes exist. Depending on the specific mineral source and the use of the product the production process may be different. Such differences were not considered. For this inventory only the caustic fusion process was investigated. To the sodium silicate by-product of this process no environmental burdens are allocated due to it's low value. This assumption also influences significantly the result for the zirconium oxide product.

97.10 Appendices: EcoSpold Meta Information

Tab. 97.7 EcoSpold Meta Information of zirconium oxide production from mineral sands

ReferenceFunction	Name	zirconium oxide, at plant		zircon production from mineral sands
Geography	Location	AU	0	AU
ReferenceFunction	InfrastructureProcess	kg	kg	kg
ReferenceFunction	Unit			
DataSetInformation	Type	1	5	
	Version	2.0	2.0	
	energyValues	0	0	
	LanguageCode	en	en	
	LocalLanguageCode	de	de	
DataEntryBy	Person	72	72	
	QualityNetwork	1	1	
ReferenceFunction	DataSetRelatesToProduct	1	1	
	IncludedProcesses	The process includes material and energy input, wastes and emissions for the production of zirconium oxide from zircon ($ZrSiO_4$) using caustic fusion with sodium hydroxide. Transport and infrastructure are estimated.		
	Amount	1	1	
	LocalName	Zirkonoxid, ab Werk	Zirkonproduktion aus Mineralsand	
	Synonyms	zirconium dioxide//zirconia		
	GeneralComment	In- and outputs of $ZrSO_4$ and $NaOH$ are calculated according to the stoichiometry. Process approximated with hydrothermal sodium silicate production and calcination of aluminium hydroxide to aluminium oxide. Weak data for energy consumption, wastes and emissions. Data partly based on a EMPA study, commissioned by the CEEs.		
	InfrastructureIncluded	1	1	
	Category	chemicals	chemicals	
	SubCategory	inorganics	inorganics	
	LocalCategory	Chemikalien	Chemikalien	
	LocalSubCategory	Anorganika	Anorganika	
	Formula	ZiO ₂		
	StatisticalClassification			
	CASNumber	001314-23-4		
TimePeriod	StartDate	2000	2000	
	EndDate	2005	2005	
	DataValidForEntirePeriod	1	1	
	OtherPeriodText			
Geography	Text	Production in Australia considered. Data bases on similar European production processes.		
Technology	Text	Caustic fusion of zircon mineral ($ZrSiO_4$) with sodium hydroxide to zirconium hydroxide. No allocation to sodium silicate by-product. Calcination of zirconium hydroxide to zirconium oxide.		
Representativeness	Percent	0.4		
	ProductionVolume	unknown	unknown	
	SamplingProcedure	Based on literature	Literature data and manufacturer information	
	Extrapolations	none	none	
	UncertaintyAdjustments	none	none	
DataGenerator	AnPerson	72	72	
	DataPublishedIn	2	2	
	ReferenceToPublishedSource	8	8	
	Copyright	1	1	
	AccessRestrictedTo	0	0	
	CompanyCode			
	CountryCode			
	PageNumbers	Zirconium oxide	Zirconium oxide	
	Validator	42	42	
	Details	automatic validation in Excel	automatic validation in Excel	
ProofReading	OtherDetails	none	none	

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