Supporting Information

What shall we do with steel mill off-gas: Optimization of polygeneration systems using steel mill off-gases to reduce greenhouse gas emissions

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43 pages including cover sheet, seven tables and two additional figures.

3 Included processes and products in the chemical industry

Table S1: List of considered chemicals and processes. The abbreviation (SC) behind a process indicates that this process is only approximated by stoichiometric inputs of the reactants and an averaged energy value obtained from a chemical park in Gendorf[1]. Processes with an asterisk (*) are aggregated processes.

name of flow	production technologies	source
1,3-propanediol	1,3-propanediol from ethylene oxide	IHS Markit[2]
	1,3-propanediol via SHELL one-step OXO process	IHS Markit[2]
	1,3-propanediol from ethylene oxide via hydroxyester	IHS Markit[2]
1,4-butanediol	1,4-butanediol from propylene oxide (allyl alcohol intermediate)	IHS Markit[2]
2,4-dimethyl benzaldehyde	2,4-dimethyl benzaldehyde from m-xylene	IHS Markit[2]
2-ethylhexanol	2-ethylhexanol by hydroformylation followed by aldol condensation and hydrogenation	IHS Markit[2]
	2-ethylhexanol from propylene, cobalt hydrocarbonyl catalyst	IHS Markit[2]
	2-ethylhexanol from propylene, cobalt phosphine catalyst	IHS Markit[2]
	2-ethylhexanol from propylene, rhodium catalyst	IHS Markit[2]

2-methyl-1,3-propanediol	co-product of '1,4-butanediol from propylene oxide (allyl alcohol intermediate)'	IHS Markit[2]
acetic acid	acetic acid by low pressure carbonylation of methanol	IHS Markit[2]
	acetic acid by the CHIYODA ACETICA process	IHS Markit[2]
	acetic acid by the CHIYODA/UOP ACETICA ™ process	IHS Markit[2]
	acetic acid from MeOH by low pressure carbonylation, supported Rh catalyst	IHS Markit[2]
	acetic acid from MeOH by the celanese process	IHS Markit[2]
	acetic acid via the BP cativa process	IHS Markit[2]
	acetic acid via the BP SAABRE process	IHS Markit[2]
	acetic acid via the celanese AO plus process	IHS Markit[2]
	acetic acid from meoh by the BP CATVIA process	IHS Markit[2]
	global market for acetoacetic acid*	ecoinvent 3.5[3]
acetone	global market for acetone, liquid*	ecoinvent 3.5[3]
acetaldehyde	co-product of 'vinyl acetate from methanol and acetic acid'	IHS Markit[2]
acetylene	acetylene production*	ecoinvent 3.5[3]

acrylic acid	acrylic acid, glacial from acetylene by catalytic process	IHS Markit[2]
acrylonitrile	acrylonitrile from propylene by ammoxidation	IHS Markit[2]
ammonia	ammonia from natural gas by steam reforming by ICI "AMV" process	IHS Markit[2]
	ammonia from N2 and H2	Kätelhön et al.[1]
benzene	methanol to benzene	IHS Markit[2]
	Low-TRL benzene from CO_2 (SC)	Kätelhön et al.[1]
	global market for benzene*	Kätelhön et al.[1]
butene	global market for butene*	ecoinvent 3.5[3]
	butene-1 from raffinate-1 by the ucc adsorption process, with deisobutanizer	IHS Markit[2]
butadiene	butadiene from n-butenes by oxidative dehydrogenation	IHS Markit[2]
	butadiene via catadiene process	IHS Markit[2]
	butadiene via tpc oxo-d process	IHS Markit[2]
calcium formate	calcium formate from lime by carbonylation	IHS Markit[2]
calcium oxide	calcium oxide*	Gabi Service Pack 39[4]
caprolactam	caprolactam from butadiene by the DUPONT-DSM process	IHS Markit[2]
	caprolactam from toluene via cyclohexane carboxylic acid	IHS Markit[2]

carbon dioxide	by direct air capture	Kätelhön et al.[1]
	ammonia from natural gas by steam reforming by ICI "AMV" process' incl CO_2 capture	Kätelhön et al.[1]
	Water gas shift reaction	IHS Markit[2]
carbon monoxide	Reverse water gas shift reaction	Artz et al.[5]
	Low-TRL CO from CO_2 (SC)	Kätelhön et al.[1]
	Carbon monoxide (via synthetic gas)	Gabi Service Pack 39[4]
chlorine	global market for chlorine, gaseous*	ecoinvent 3.5[3]
cooling energy	cooling energy, from natural gas, at cogen unit with absorption chiller 100kW*	ecoinvent 3.5[3]
	global market for water, decarbonized, at user*	ecoinvent 3.5[3]
cumene	cumene from benzene and propylene	IHS Markit[2]
cyclohexane	global market for cyclohexane*	ecoinvent 3.5[3]
dimethyl carbonate	Oxidative carbonylation (Eni-) process	Artz et al.[5]
	Ethylene carbonate Route A1	Artz et al.[5]
	Ethylene carbonate Route A2	Artz et al.[5]
	Urea transformation Route B	Artz et al.[5]
	Ethylene carbonte - MIBK Route	Artz et al.[5]
	Ethylene carbonte - EG Route	Artz et al.[5]

	dimethyl carbonate by liquid-phase oxidative carbonylation	IHS Markit[2]
	dimethyl carbonate by vapor-phase oxidative carbonylation	IHS Markit[2]
diphenyl carbonate	diphenyl carbonate by direct phosgenation with fixed-bed reactors	IHS Markit[2]
	diphenyl carbonate from phenol by oxidative carbonylation using fixed-bed reactors	IHS Markit[2]
	diphenyl carbonate from phenol via dpo with ube technology	IHS Markit[2]
	diphenyl carbonate production by a phosgene process	IHS Markit[2]
	diphenyl carbonate production by a process similar to ge process	IHS Markit[2]
	diphenyl carbonate production by a process similar to ube process	IHS Markit[2]
	diphenyl carbonate via dimethyl carbonate by oxidative carbonylation and reactive distillation	IHS Markit[2]
electricity	EU-28: Electricity from wind power ts*	Gabi Service Pack 39[4]
	EU-28: Electricity from grid mix (2020)*	Gabi Service Pack 39[4]
	manually variated impact to analyse the influence	

ethylbenzene	ethylbenzene by badger EBMAXÂ™ liquid phase alkylation proces	IHS Markit[2]
	ethylbenzene from benzene by liquid-phase alkylation, zeolite cat.	IHS Markit[2]
ethylene	Low-TRL ethylene from CO_2 via CH4 (SC)	Kätelhön et al.[1]
	ethylene by the UOP/HYDRO methanol to olefins process	IHS Markit[2]
	Low-TRL ethylene from CO_2 via H2 (SC)	Kätelhön et al.[1]
	global market for ethylene*	ecoinvent 3.5[3]
ethylene carbonate	ethylene carbonate production	ecoinvent 3.5[3]
ethylene glycol	ethylene glycol from ethylene oxide by thermal hydration	IHS Markit[2]
	ethylene glycol production from syngas by SINOPEC process	IHS Markit[2]
ethylene oxide	Low-TRL ethylene oxide from CO_2 (SC)	Kätelhön et al.[1]
	ethylene oxide from ethylene by oxygen oxidation (all marketable ethylene oxide)	IHS Markit[2]
formic acid	CO_2-based formic acid production (values per kg pure formic acid) Ia (Pérez-Fortes et al.)	Artz et al.[5]

	CO$_2$-based formic acid production (values per kg pure formic acid) Ib (Jens et al.)	Artz et al.[5]
	formic acid (85%) by BASF process	IHS Markit[2]
	formic acid (85%) by HALCON/SD process	IHS Markit[2]
	formic acid (85%) by LEONARD process	IHS Markit[2]
	formic acid (85%) via improved KEMIRA process	IHS Markit[2]
formaldehyde	formaldehyde from methanol by the TOPSOE SR process	IHS Markit[2]
	formaldehyde from methanol, ferric-molybdate catalyst	IHS Markit[2]
	formaldehyde from methanol, silver catalyst	IHS Markit[2]
heat	power to heat ($\eta = 95$ %)	Artz et al.[5]
	EU-28: Thermal energy from natural gas ts	Gabi Service Pack 39[4]
hydrochlorid acid	market for hydrochloric acid*	ecoinvent 3.5[3]
hydrogen	GLO: Electrolysis with wind, 50 (kW h)/ kg of H2 ts	Götz et al.
	hydrogen from natural gas by steam reforming	IHS Markit[2]
	Water gas shift reaction	IHS Markit[2]

hydrogen cyanide	global market for hydrogen cyanide*	ecoinvent 3.5[3]
incineration of steel mill off-gases	treatment of blast furnace gas, in power plant	ecoinvent 3.5[3]
	treatment of coal gas, in power plant	ecoinvent 3.5[3]
isobutanol	co-product of '2-ethylhexanol from propylene, cobalt hydrocarbonyl catalyst'	IHS Markit[2]
	co-product of '2-ethylhexanol from propylene, cobalt phosphine catalyst'	IHS Markit[2]
inert gas	European market for nitrogen, liquid*	ecoinvent 3.5[3]
isobutylene	global market for butene, mixed*	ecoinvent 3.5[3]
isobutyraldehyde	co-product of 'n-butanol from propylene via n-butyraldehyde, rhodium catalyst'	IHS Markit[2]
	co-product of 'n-butyraldehyde by the oil-soluble phosphine process with dual reactors'	IHS Markit[2]
	co-product of 'n-butyraldehyde by the water-soluble phosphine process with a secondary reactor'	IHS Markit[2]
	co-product of 'n-butyraldehyde from propylene (water-sol rh catalyst)'	IHS Markit[2]

	co-product of 'n-butyraldehyde from propylene by the phosphite process with c3 absorption'	IHS Markit[2]
	co-product of 'n-butyraldehyde from propylene via LP OXO process with liquid recycle'	IHS Markit[2]
	co-product of 'n-butyraldehyde production by LP OXO selector process'	IHS Markit[2]
lime	global market for lime*	ecoinvent 3.5[3]
methane	Methane from CO_2 (de Saint Jean et al.)	Artz et al.[5]
	Methane from CO_2 (Müller et al.)	Artz et al.[5]
	Methane from purification of natural gas	Gabi Service Pack 39[4]
methanol	Methanol from CO_2 (from JRC)	Artz et al.[5]
	CO_2-based methanol synthesis	Artz et al.[5]
	CO_2-based methanol production (values per kg methanol) IVa (Rhiko-Struckmann et al.)	Artz et al.[5]
	CO_2-based methanol production (values per kg methanol) IVb (Van Dal et al.)	Artz et al.[5]
	CO_2-based methanol production (values per kg methanol) IVc (Kiss et al.)	Artz et al.[5]
	methanol (mega scale) from syngas via LURGI technology	IHS Markit[2]

	methanol (mega scale) via LURGI technology	IHS Markit[2]
methyl methacrylate	methyl methacrylate via EASTMAN technology (C2 based)'	IHS Markit[2]
	methyl methacrylate via LUCITE technology (C2 based)'	IHS Markit[2]
methyl t-butyl ether	MTBE production integrated with n-butene isomerization and petrochemical plant process	IHS Markit[2]
	methyl tert-butyl ether production*	ecoinvent 3.5[3]
natural gas	European natural gas mix*	Kätelhön et al.[1]
nitric oxide	nitric oxide production*	ecoinvent 3.5[3]
nitrogen	European market for nitrogen, liquid*	ecoinvent 3.5[3]
n-butane	butane production mix*	Gabi Service Pack 39[4]
n-butanol	n-butanol from propylene via n-butyraldehyde, rhodium catalyst	IHS Markit[2]
	n-butanol from propylene, cobalt hydrocarbonyl catalyst	IHS Markit[2]
	n-butanol from propylene, cobalt-phosphine catalyst	IHS Markit[2]
n-butyraldehyde	n-butyraldehyde by the oil-soluble phosphine process with dual reactors	IHS Markit[2]

	n-butyraldehyde by the water-soluble phosphine process with a secondary reactor	IHS Markit[2]
	n-butyraldehyde from propylene (water-sol rh catalyst)	IHS Markit[2]
	n-butyraldehyde from propylene by the phosphite process with C3 absorption	IHS Markit[2]
	n-butyraldehyde from propylene via lp oxo process with liquid recycle	IHS Markit[2]
	n-butyraldehyde production by lp oxo selector process	IHS Markit[2]
octene	1-octene production by ethylene tetramerization process	IHS Markit[2]
oleum	mixing of sulfur trioxide and sulfuric acid	Kätelhön et al.[1]
oxygen	European market for oxygen, liquid*	ecoinvent 3.5[3]
phenol	phenol from cumene via oxygen-based liquid oxidation	IHS Markit[2]
phosgene	phosgene from chlorine and carbon monoxide by active carbon catalysis	IHS Markit[2]
polycarbonate	Polycarbonate (PC) units	Artz et al.[5]
	CO-based polycarbonate	own assessment
	Polycarbonate via phosgenation of Bisphenol A	own assessment

polyether units	Polyether (PE) units	Artz et al.[5]
polyethylene	polyethylene, HD, by gas phase fluidized-bed process (UCC)	IHS Markit[2]
	polyethylene, lLD by a high pressure autoclave process	IHS Markit[2]
	polyethylene, LLD, by a medium pressure solution process (DUPONT technology)	IHS Markit[2]
polyol	CO_2-based polyol production	Artz et al.[5]
	polyol production*	ecoinvent 3.5[3]
polypropylene	polypropylene homopolymer by a vertical stirred bed gas phase process (BASF)	IHS Markit[2]
process water	global market for water, decarbonized, at user*	ecoinvent 3.5[3]
propylene	methanol to olefins by the DMTO process	IHS Markit[2]
	methanol to olefins by the DMTO-II process	IHS Markit[2]
	methanol to olefins by the DMTO-II process - modified	IHS Markit[2]
	methanol to propylene by the LURGI MTP process	IHS Markit[2]
	methanol to propylene by the LURGI MTP process updated	IHS Markit[2]

	Low-TRL propylene from CO_2 (SC)	Kätelhön et al.[1]
	global market for propylene*	ecoinvent 3.5[3]
propylene oxide	propylene oxide by the conventional chlorohydrin process	IHS Markit[2]
sodium	market for sodium*	ecoinvent 3.5[3]
starter (glycerol)	glycerine production, from epichlorohydrin*	ecoinvent 3.5[3]
steam	steam (medium pressure) production from packaged gas boiler	IHS Markit[2]
	combustion of natural gas	Kätelhön et al.[1]
	venting of overproduced steam	Kätelhön et al.[1]
styrene	Low-TRL styrene from CO_2 (SC)	Kätelhön et al.[1]
	styrene from benzene and ethylene via liquid-phase alkylation and oxidative reheat	IHS Markit[2]
	styrene from benzene and ethylene via vapor-phase alkylation and adiabatic dehydrogenation	IHS Markit[2]
sulfur trioxide	global market for sulfur trioxide*	ecoinvent 3.5[3]
sulfuric acid	global market for sulfuric acid*	ecoinvent 3.5[3]
synthesis gas	CO_2-based carbon monoxide production via rWGS (valus per kg CO) IIa - electrically heated reactor (CO_2RRECT)	Artz et al.[5]

	CO_2-based carbon monoxide production via rWGS (valus per kg CO) IIb - reactor heated by steam	Artz et al.[5]
	CO_2-based carbon monoxide production via DRM (valus per kg CO) IIa - electrically heated reactor (CO_2RRECT)	Artz et al.[5]
	CO_2-based carbon monoxide production via DRM (valus per kg CO) IIb - reactor heated by steam	Artz et al.[5]
	separation/treatment of steel mill off-gases	own calculations
	mixing of hydrogen and carbon monoxide to adjust mixing rations	own calculations
terephthalic acid	terephthalic acid, purified, by the conventional catalytic air oxidation process	IHS Markit[2]
thermal energy	production of thermal energy from various feedstock: fuel oil, fuel gas, C1-C2 purge, C4-C5 purge, liquid-petroleum gas, methane, methanol, natural gas, propane, residual fuel oil, propylene	Kätelhön et al.[1]
toluene	methanol-to-aromatics	Kätelhön et al.[1]
	Low-TRL toluene from CO_2 (SC)	Kätelhön et al.[1]
	global market for toluene*	ecoinvent 3.5[3]

toluene diisocyanate	Low-TRL CO_2-based TDI	own assessment
	TDI via phosgenation of TDA	own assessment
urea	urea by the SAIPEM/SNAMPROGETTI process	IHS Markit[2]
	urea by the STAMICARBON UREA 2000PLUS process	IHS Markit[2]
	urea by UTIS heat recycle process	IHS Markit[2]
	urea, agricultural grade, by the isobaric double recycle process	IHS Markit[2]
	urea, agricultural grade, by the MITSUI TOATSU process	IHS Markit[2]
vinyl acetate	vinyl acetate from methanol and acetic acid	IHS Markit[2]
vinyl chloride	vinyl chloride by a balanced process with heat and HCl recovery (oxy vinyls)	IHS Markit[2]
carbon waste flow	carbon waste streams calculated according to Kätelhön et al.[1] et al. 2019	Kätelhön et al.[1]
waste water	Municipal waste water treatment*	Gabi Service Pack 39[4]
water	Water (desalinated; deionized)*	Gabi Service Pack 39[4]
xylene (mixed)	methanol to xylene (ortho)	Kätelhön et al.[1]

	Low-TRL xylene (ortho) from CO_2 (SC)	Kätelhön et al.[1]
	global market for xylene*	ecoinvent 3.5[3]
xylene (para)	methanol to xylene (para)	Kätelhön et al.[1]
	Low-TRL xylene (para) from CO_2 (SC)	Kätelhön et al.[1]
	p-xylene by a PAREX(R)/MHAI process	IHS Markit[2]

Table S2: Market capacities of the considered chemical products

Product	Mt/year	year	Reference
1,3-propanediol	0.146	2014	Grand View Research[6]
1,4-butanediol	2	2025	Burgard et al.[7]
2-ethylhexanol	4	2018	Markets and Markets[8]
Acetic acid	13	2013	Pal and Nayak[9]
Acetaldehyde	2	2009	Jira[10]
Acetylene	0.4	2012	Getman et al.[11]
Acrylic acid	5.85	2014	Market Research Store[12]
Calcium formate	0.695	2018	Transparency Market Research[13]
Cyclohexane	9.19	2016	Grand View Research[14]
Dimethyl carbonate	0.09	2002	Cavani[15]
Diphenyl carbonate	0.254	2002	Wikipedia[16]
Ethylbenzene	37	2012	Al-Kinany and Aldrees[17]
Formic acid	0.76	2019	Pérez-Fortes et al.[18]
Formaldehyde	20.9	2006	Duong et al.[19]
Isobutanol	0.552	2014	Grand View Research[20]
Isobutylene	15	2015	Vaz Jr[21]
Isobutyralaldehyde	1	2000	Cornils et al.[22]
Methyl formate	0.002	2002	PubChem[23]
Methyl methacrylate	3.5	2008	PubChem[24]
n-butanol	3.8	2012	Jiang et al.[25]
n-butyraldehyde	7	2013	Ku et al.[26]
Octene	0.609	2006	ICIS - Independent Commodity Intelligence Services[27]
Phosgene	6	2003	Cotarca and Eckert[28]
Vinyl acetate	6.97	2007	Wikipedia[29]

Table S3: Production volumes of the considered chemical products

Product	Mt/year	year	Reference
Acetone	10.68	2030	Kätelhön et al.[1]
Acrylonitrile	10.42	2030	Kätelhön et al.[1]
Ammonia	229.17	2030	Kätelhön et al.[1]
Benzene	65.97	2030	Kätelhön et al.[1]
Caprolactam	3.48	2030	Kätelhön et al.[1]
Cumene	24.32	2030	Kätelhön et al.[1]
Ethylene	250.01	2030	Kätelhön et al.[1]
Ethylene glycol	41.66	2030	Kätelhön et al.[1]
Ethylene oxide	41.66	2030	Kätelhön et al.[1]
Methanol	134.42	2030	Kätelhön et al.[1]
Phenol	17.35	2030	Kätelhön et al.[1]
Polycarbonate	5.1	2016	Plastics Insight[30]
Polyethylene	163.19	2030	Kätelhön et al.[1]
Polyol	9.4	2016	Statista[31]
Polypropylene	100.71	2030	Kätelhön et al.[1]
Propylene	139.18	2030	Kätelhön et al.[1]
Propylene oxide	13.89	2030	Kätelhön et al.[1]
Styrene	48.61	2030	Kätelhön et al.[1]
Terephthalic acid	100.69	2030	Kätelhön et al.[1]
Toluene	34.7	2030	Kätelhön et al.[1]
Toluene diisocyanate	3.36	2019	ECTC Chemical Technologies[32]
Urea	197	2022	International Fertilizer Association[33]
Vinyl chloride	55.56	2030	Kätelhön et al.[1]
Xylene (mixed)	93.74	2030	Kätelhön et al.[1]
Xylene (para)	69.45	2030	Kätelhön et al.[1]

Mass flows in the optimized chemical industry

The chemical industry is optimized for the *today* and the *future* electricity scenario. The optimized chemical industries are compared to the *business-as-usual* benchmark in Figure S1 and Figure S2, respectively. For reasons of clarity, only the mass flows that are changed by the optimization of the chemical industry are shown. In contrast to optimization proposed by Kätelhön et al.[1], where the methanol-to-olefin processes only became ecologically advantageous for the electricity supply from a carbon footprint of 124 - 219 g CO_2 equivalents/kWh, in this study these processes are already advantageous in the today scenario.
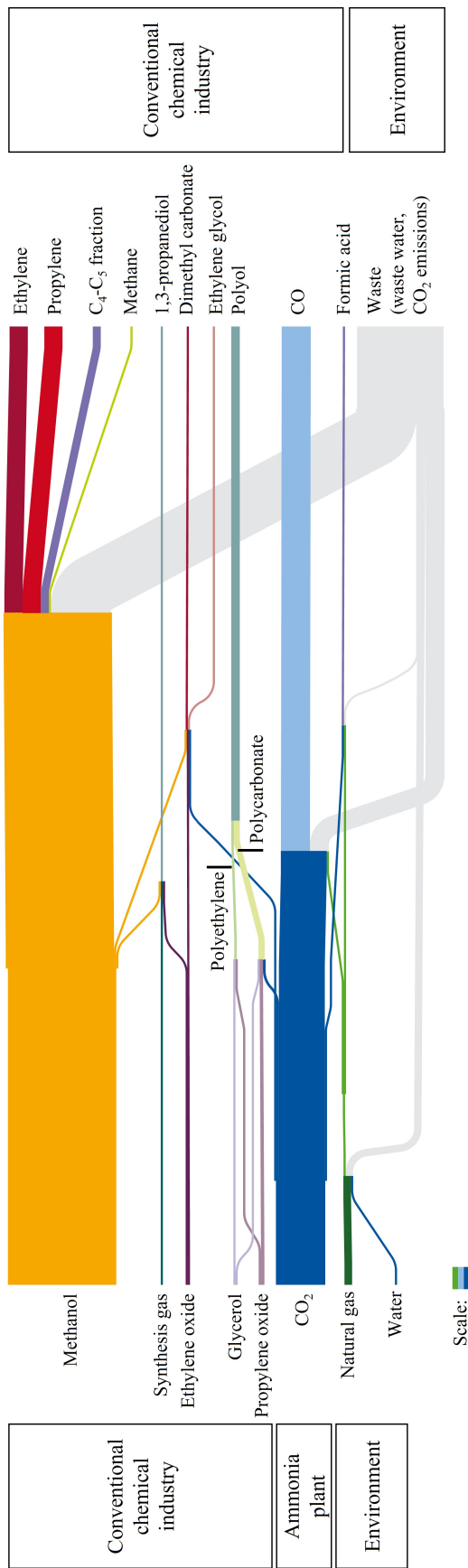
Figure S1: Mass flows in the optimized chemical industry using the *today* electricity scenario. A reference flow, consisting of 3 x 5 Mt, is given at the bottom left as a scale.

This is due to the fact that in the process *Ethylene by the UOP/Hydro methanol to olefins* a C_4-C_5 fraction is co-produced. The combustion of this fuel gas provides heat with lower GHG emissions than the combustion of natural gas and is thus used for heat integration with other processes within this optimized chemical industry. Furthermore, the production of CO_2-based dimethyl carbonate, polyol, carbon monoxide and formic acid becomes climate beneficial.

Steel mill off-gas compositions

Amount and properties of the generated steel mill off-gases influence the subsequent utilization. In this paper, we assume the off-gas streams as steady-state and the respective input stream parameters are characterized in Table S4. Because of the similar compositions and the low quantity of generated BOFG, we aggregate BFG and BOFG into one stream. Pollutions such as metals in the steel mill off-gases are neglected since these substances must be separated already today before the steel mill off-gases can be used[34]. The separation processes such as electrostatic precipitators with their related GHG emissions are thus similar for all regarded scenarios and can be allocated to the steel mill itself outside the system boundaries.

Combustion Processes

Today, steel mill off-gases are combusted for re-heating and power generation. Accordingly, we include this utilization pathway in the integrated model. Since the steel mill and thus the heat integration with the steel mill is excluded from the model, we consider the combustion in combined heat and power plants (CHP). The linear combustion processes are shown in Table S5.

When steel mill off-gases are utilized for chemical production, the resulting demand of heat and electricity is settled from other sources. Accordingly, we consider an annual demand
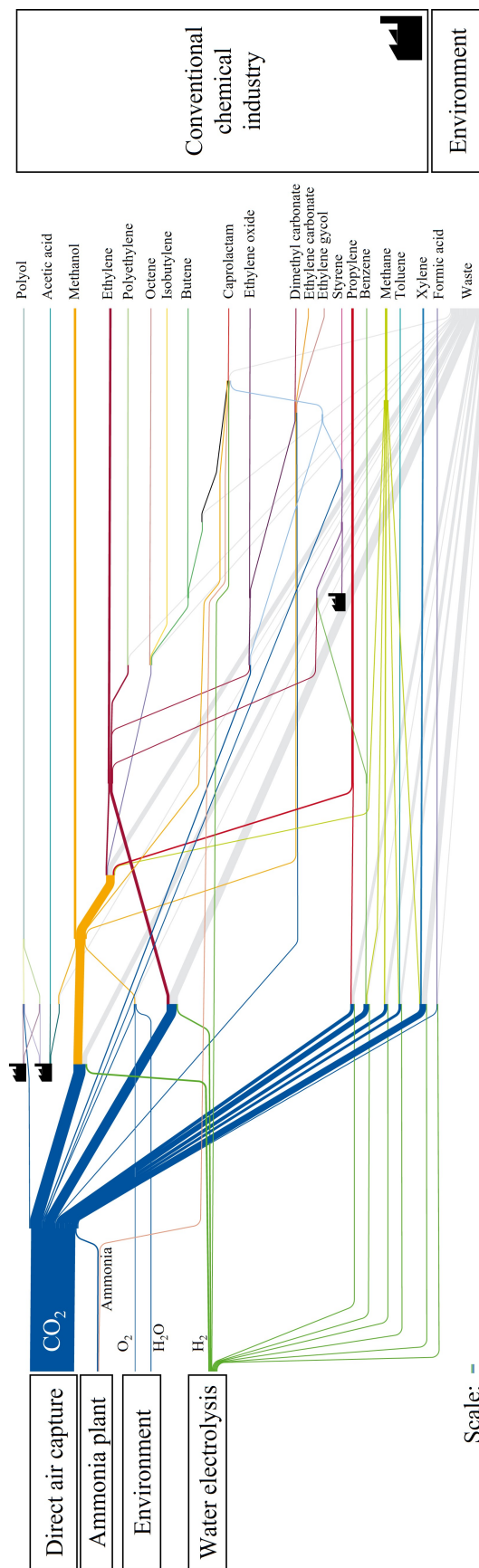
Figure S2: Mass flows in the optimized chemical industry using the *future* electricity scenario. A reference flow, consisting of 3 x 5 Mt, is given at the bottom left as a scale.

Table S4: Quantity and properties of the annual, worldwide steel mill off-gas streams. Molar compositions are adapted from Uribe-Soto et al.[35], mass streams are obtained from own calculations.

	in	COG	BFG	BOFG	BFG/BOFG mix
m	Mt/year	39.70	-	-	1740.55
t	°C	30	30	30	30
p	bar	1	1	1	1
M	g/mol	8.94	-	-	30.11
Component k		Mole fractions y_k			
CO_2		0.012	0.22	0.2	0.21
CO		0.042	0.24	0.54	0.24
H_2		0.621	0.04	0.03	0.065
$CH4$		0.225	0	0.3	0.011
N_2		0.059	0.47	0.18	0.436
H_2O		0.041	0.04	0	0.04

of 248 TWh heat and 638 TWh electricity in the polygeneration system, corresponding to the complete combustion of the steel mill off-gas streams in the CHP.

Unit Operations for the Separation System

The unit operations considered in the separation system are chosen according to the work proposed by Ghanbari et al.[36]. Both steel mill off-gases are mixtures of different chemical

Table S5: Combustion processes for steel mill off-gases[3]

Interm. Flow	in	Combustion COG in CHP	Combustion BFG/BOFG in CHP
BFG/BOFG	kg	0	-0.370
COG	kg	-0.027	0
Electricity	MJ	0.396	0.365
Heat	MJ	0.145	0.145
Water	kg	0.206	-0.177
GWI	kg CO_2-eq	0.263	0.036

components. Although first approaches are presented in the literature, utilizing the raw steel mill off-gas as feedstock, e.g. Thonemann and Maga[37], the separation of these gas mixtures is inevitable for the subsequent chemical utilization in the presented model. In the following section, we present the used unit operations for the separation steps according to the work proposed by Ghanbari et al.[36].

Absorption and adsorption processes are among those unit operations. The target component is selectively removed from the gas mixture through chemical or physical binding. While absorption refers to the transfer into a liquid solvent, adsorption refers to the interaction at a solid surface. Both mechanisms prefer low temperatures and high pressures. In the subsequent desorption step, the binding is released and the target component is recovered in gaseous state. For desorption, high temperatures and low pressures are favourable. Additionally, chemical reactions are performed to convert the components. Those reactions include the reforming of CH_4 and the conversion of CO to CO_2 and H_2.

Pressure Swing Adsorption

Pressure swing adsorption (PSA) exploits the pressure dependence of the adsorption equilibrium. The adsorption step is performed at high pressure levels. Through binding to the solid material (adsorbent) surface, target component is removed from the gas mixture. Compressing the feed gas stream requires energy. Accordingly, the feed compressor power is the main energy cost of the process. The desorption step is conducted subsequently. By lowering the pressure, the target component leaves the adsorbent surface and is recovered in gaseous state[38].

Continuous operation of the PSA process requires a two-unit arrangement (Figure S3). The circulation of the solid adsorbent between two pressure levels is hard to conduct in practice. Instead, the adsorbent bed is fixed in two columns. The two beds alternate between adsorption and desorption phases to enable a continuous process. Only one column at a time is connected to the feed and by-product stream, therefore representing the adsorption

68 column. In the fixed adsorbent bed of column 1, the target component accumulates. When

69 the adsorbent is saturated, column 1 is disconnected from feed and by-product stream and

70 connected to the product stream. Now, the desorption step takes place in column 1. The

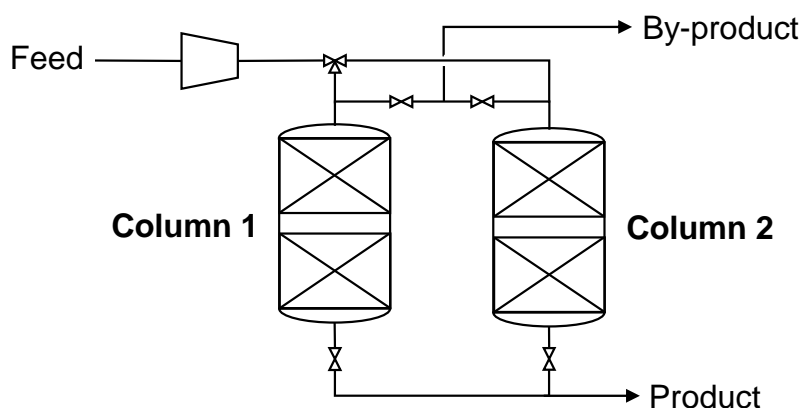71 respective opposite step occurs simultaneously in the column 2[39].

Figure S3: Basic flowsheet of the continous pressure swing adsorption process (PSA)

72 The PSA process is suitable for two tasks in steel mill off-gas separation: First, the

73 recovery of H_2 from COG, BFG and BOFG[35,40]. Second, the recovery of CO_2 from BFG

74 and BOFG. Kim et al.[41] presented a detailed study on the application of PSA to recover

75 CO_2 from steel mill off-gas streams.

Temperature Swing Adsorption

77 Temperature swing adsorption (TSA) exploits the temperature dependency of the adsorption

78 equilibrium. The adsorption step is performed at moderate temperatures. For the desorption

79 step, the temperature is increased. Subsequently, the target component is released. Heating

80 the product-enriched adsorbent is the greatest operational energy requirement of this pro-

[81] cess[38]. Ghanbari et al.[36] suggested TSA for the recovery of CO from BFG and BOFG. Rabo

[82] et al.[42] investigated the adsorption behaviour of CO on zeolitic molecular sieves. While the

[83] adsorption process showed a strong temperature dependence, no significant pressure depen-

[84] dency was observed. Accordingly, TSA was found suitable for CO recovery.

Chemical Absorption

[86] The main concept of chemical absorption is the transfer of the gaseous target component

[87] into a liquid solvent (absorbent). Chemical reactions take place in the liquid phase, thereby

[88] retaining the target component. In the subsequent desorption step, the reactions are reversed

[89] by temperature changes. The target component is stripped from the solvent and recovered
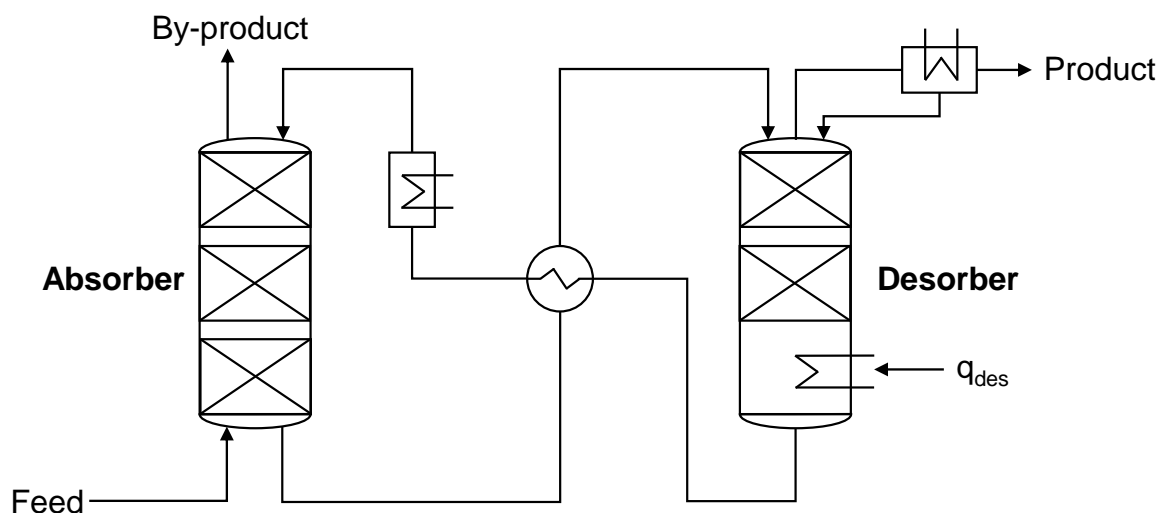
[90] as gaseous product.

Figure S4: Basic flowsheet of the chemical CO_2 absorption process

[91] Chemical absorption (CCA) with aqueous monoethanolamine (MEA) solutions is the

[92] conventional set-up for removing CO_2 from gas streams[43]. Figure S4 shows the main units

[93] of this separation process. The absorber is operated at temperatures around 40°C. The

lean solvent enters at the top and flows countercurrently to the feed gas stream through the column. The product-enriched solvent is drained at the bottom and sent to the desorber. As the desorption step takes place at elevated temperatures (around 120°C), the rich solvent is pre-heated by the lean solvent stream leaving the desorber. Main energy cost of the chemical absorption process is the desorption heat, supplied in the desorber bottom. Because of the elevated temperatures, water evaporates from the MEA solution. To obtain a pure product, this water is removed from the product gas stream in a condenser at the column top[41,44].

Membrane Separation Process

Membrane separation processes (MSP) are investigated as alternative to the conventional gas separation processes. Key element is the membrane, beeing selectively permeable to the target component. The feed gas stream enters the membrane module at elevated pressure and flows along the membrane. By passing through the membrane, the target component is enriched with the product stream (permeate). The by-product stream (retentate) leaves the module without passing the membrane. Lower energy requirements are the most prominent advantage of membrane separation processes[38]. However, limited product purities are the main drawback[41]. To obtain a product stream of sufficient quality, multiple membrane stages are often required. Moreover, purity and product recovery form a trade-off. Higher feed pressures force more gas through the membrane, increasing the product recovery rate. At the same time, the product purity decreases[35].

Two steps in the separation of steel mill off-gases can be conducted with membrane separation processes: First, the recovery of H_2 from COG, BFG and BOFG. Second, the recovery of CO_2 from BFG and BOFG[35,36]. Lie et al.[45] presented a detailed study on the recovery of CO_2 from steel mill off-gases with a fixed-site-carrier membrane.

Water Gas Shift Reaction

The water-gas-shift reaction (WGSR) enhances the flexibility of the separation system: Under addition of steam (H_2O), CO is converted into H_2 and CO_2 by the equilibrium reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \qquad \Delta H_R = -41.1\,\text{kJ mol}^{-1} \qquad (1)$$

Thereby, the ratio of the three products is adjusted to fulfill the demands of the subsequent utilization. The reaction enthalpy is denoted by ΔH_R. According to Le Chatelier's principle, low temperatures raise the equilibrium product concentration of the exothermic reaction. However, the reaction slows at low temperatures. To adress this trade-off between kinetics and equilibrium, several operation modes are applied. For the WGSR of steel mill off-gases, the low-temperature shift reaction (LTSR) operated at 200 - 300 °C over Cu-Zn catalysts was found promising[46].

Methane Reforming

Methane reforming decomposes CH_4 into H_2 and CO. Many chemical production processes consume this product mixture, referred to as synthesis gas (syngas). The ratio between both components varies for each process and is therefore an important property. syngas 2:1 denotes a molar H_2-to-CO-ratio of 2:1. Three reaction pathways can be applied to methane reforming:

Steam methane reforming

Steam methane reforming (SMR) is the conventional reaction pathway. However, the strong endothermic SMR consumes large amounts of heat. The product mixture contains comparatively high amounts of H_2, resulting in syngas 3:1 (Equation 2). Simultaneos to the SMR, the WGSR takes place.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad\qquad \Delta H_R = 234.7\,\text{kJ}\,\text{mol}^{-1} \qquad (2)$$

Partial oxidation reforming

Partial oxidation reforming (POR) is slightly exothermic and therefore beneficial in terms of energy consumption. However, the reaction requires pure oxygen (O_2) as co-reactant.

$$CH_4 + 0.5O_2 \rightleftharpoons CO + 2H_2 \qquad\qquad \Delta H_R = -35.9\,\text{kJ}\,\text{mol}^{-1} \qquad (3)$$

The oxygen supply leads to additional costs. Syngas 2:1 is obtained as product stream, the optimal composition for most subsequent production processes[47].

Carbon dioxide reforming

Carbon dioxide reforming (CDR) utilizes CO_2 as co-reactant. Therefore, CDR is considered as CCU technology. Heat is supplied to perform the strongly endothermic reaction step. Syngas 1:1 is produced, according to the stoichiometry[48].

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad\qquad \Delta H_R = 247\,\text{kJ}\,\text{mol}^{-1} \qquad (4)$$

Flowsheet of the separation superstructure

We use a fixed sequence and connectivity of the separation steps, adapted from Ghanbari et al.[36]

The first step of the COG separation (see Figure S5) is the H_2 recovery. MSP or PSA are applied for this task. For both pressure-driven units, an upstream compressor is required. The by-product stream contains mainly CH_4, which can either be utilized (Stream 35) or converted. To produce syngas, Stream 37 supplies the co-reactant (CO_2, H_2O or

¹⁵² O_2). Subsequently, the mixture is sent to the methane-reforming unit. Three reactions are

¹⁵³ applicable to this task: SMR, CDR and POR. Dependent on the selected reaction, heat is

¹⁵⁴ consumed or produced. All three reactions are operated at high conversion rates (see Table

¹⁵⁵ S7). Accordingly, output stream 40 is assumed as pure syngas.
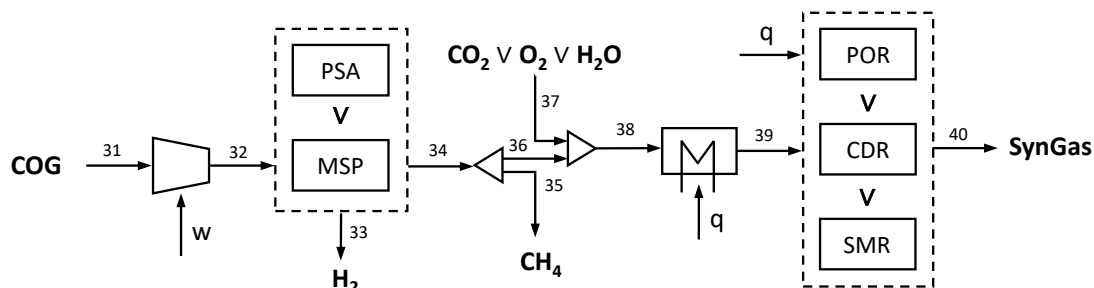
Figure S5: Superstructure of the COG separation system

¹⁵⁶ The BFG/BOFG mixture contains large amounts of CO (see Table S4). Thus, CO

¹⁵⁷ recovery is performed via TSA as first step (Figure S6). Recovered CO is either utilized

¹⁵⁸ (Stream 20) or converted. For the WGSR step, steam (H_2O) is supplied as co-reactant

¹⁵⁹ (Stream 22). The resulting gas mixture is heated and sent to the reactor. Through the

¹⁶⁰ WGSR step, additional H_2 and CO_2 can be obtained. Since the reactor output stream (25)

¹⁶¹ and the TSA by-product stream (4) both consist of H_2 and CO_2 in similar compositions,

¹⁶² the streams are mixed to conduct the CO_2 separation subsequently.
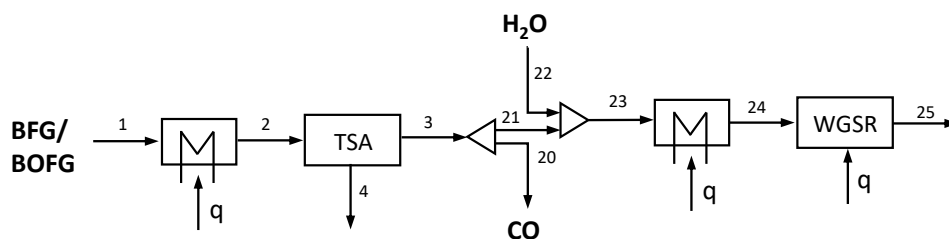
Figure S6: Superstructure of the BFG/BOFG separation system (1/2)

¹⁶³ Three unit alternatives can perform the subsequent CO_2 recovery: MSP, PSA or CCA

(see Figure S7). Through a heat exchanger and a compressor, the operating conditions for the selected process a generated. Last step of the BFG/BOFG separation is another H_2 recovery step. The by-product stream of this unit (12) contains large amounts of N_2, but also unrecovered gas components. Accordingly, the stream is considered as waste and passed to the linear model of the chemical industry. There, the stream is released to the atmosphere, and the GHG emissions of environmentally relevant gases, in particular CO and CO_2 , are considered in the objective function.
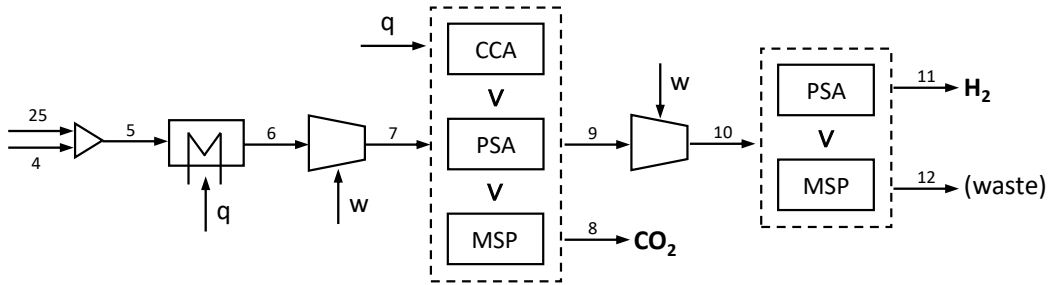

Figure S7: Superstructure of the BFG/BOFG separation system (2/2)

Model equations and parameters for the separation superstructure

In the following section, equations and parameters used for the separation system model are presented.

Heat exchanger and compressor

Energy demands for heat exchangers and compressors are calculated by energy balances:

$$q_{HE} = n^{in}(h^{out} - h^{in})/\eta_{HE} \tag{5}$$

$$w_{comp} = n^{in}(h^{out} - h^{in})/\eta_{comp} \tag{6}$$

The efficiencies are set to $\eta_{\mathrm{comp}} = 0.7$ and $\eta_{\mathrm{HE}} = 0.7$[36].

Thermodynamic properties

Pure substance enthalpies for all mill gas components are estimated by the Shomate Equation:

$$h_k(T) = B_{1k} + B_{2k}\frac{T^2}{2} + B_{3k}\frac{T^3}{3} + B_{4k}\frac{T^4}{4} - \frac{B_{5k}}{T} + B_{6k} - B_{7k} \tag{7}$$

Coefficients B_{1k} - B_{7k} are obtained from the NIST chemical webbook[49]. Enthalpy of each stream is calculated under assumption of an ideal gas mixture similar to Ghanbari et al.[36]:

$$h^i = \sum_k h_k(T^i)y_k^i \tag{8}$$

Isentropic relation for ideal gas:

$$\frac{T^{\mathrm{out}}}{T^{\mathrm{in}}} = \frac{p^{\mathrm{out}}}{p^{\mathrm{in}}}^{\frac{\kappa-1}{\kappa}} \tag{9}$$

with heat capacity ratio κ and gas constant R:

$$\kappa = \frac{C_p}{C_p - R} \tag{10}$$

The molar heat capacities C_p are calculated with the derivative of the Shomate Equation 7.

Pressure Swing Adsorption

Following shortcut equation is used to calculate the product recovery from the pressure ratio. The adsorbent selectivity is denoted by β[50]:

$$\frac{p^{\mathrm{prod}}}{p^{\mathrm{in}}} = y_{k_{\mathrm{prod}}}^{\mathrm{in}}\left(1 - \frac{\zeta_{k_{\mathrm{prod}}}}{1 - \beta}\right) \tag{11}$$

For hydrogen recovery ($k_{\mathrm{prod}} = H_2$), a selectivity of $\beta_{H_2} = 0.02$ is used[36]. For carbon dioxide recovery ($k_{\mathrm{prod}} = CO_2$), Equation 11 was fitted to operational data from Kim et al.[41],

resulting in $\beta_{CO_2} = 0.024$. The product stream is assumed to be pure target component $(y_{k_{\text{prod}}}^{\text{prod}} = 1)$.

Temperature Swing Adsorption

Similar to the PSA, the product stream is assumed as pure target component. Through a mass balance with adsorbent stream m_{ads}, the product flow is determined. X^{rich} and X^{lean} denote rich and lean adsorbent mass loadings.

$$m_{\text{ads}}(X^{\text{rich}} - X^{\text{lean}}) = M_{CO}\, n^{\text{prod}} y_{CO}^{\text{prod}} \tag{12}$$

As main energy requirement, the desorption heat q_{des} is calculated. Because of very small loadings, adsorption enthalpy and product heating are neglected.

$$q_{\text{des}} = m_{\text{ads}} c_{p,\text{ads}}(t_{\text{des}} - t_{\text{ads}}) \tag{13}$$

Adsorption isotherms from Rabo et al.[42] at $t_{\text{ads}} = 50°C$ and $t_{\text{des}} = 250°C$ are used to determine rich and lean loadings. The adsorbent (zeolite 13X) heat capacity $c_{p,\text{ads}} = 1.34\,\text{kJ}\,\text{kg}^{-1}\,\text{K}^{-1}$ was obtained from Kakavandi et al.[51].

Chemical Absorption

The desorption heat for the chemical absorption process of CO_2 with MEA is estimated with an empirical correlation from Kim et al.:[41]

$$q = 4.2 n^{\text{prod}} M_{CO_2} \tag{14}$$

The product recovery is constrained by $\zeta_{CO_2} \leq 0.9$. The process is operated at fixed temperatures $t_{\text{des}} = 120°C$ and $t_{abs} = 40°C$ and and a pressure of 1.5 bar. A more advanced shortcut model by Ralf Notz et al.[44], based on the Kremser Equation, was also tested but

209 impaired overall convergence.

Membrane Separation Process

211 The shortcut equations for the MSP are adapted from Ghanbari et al.[36]. Product recovery:

$$\frac{p^{\text{prod}}}{p^{\text{in}}} = \left(\frac{y_{k_{\text{prod}}}^{\text{in}}}{y_{k_{\text{prod}}}^{\text{prod}}}\right)\left(\frac{1-\zeta_{k_{\text{prod}}}}{1-y_{k_{\text{prod}}}^{\text{in}}\zeta_{k_{\text{prod}}}}\right) \tag{15}$$

212 Mole fraction of k in the product stream:

$$n^{\text{prod}}y_k^{\text{prod}} = \frac{\alpha_{k/k_{\text{prod}}}\zeta_{k_{\text{prod}}}y_k^{\text{in}}y_{k_{\text{prod}}}^{\text{in}}n^{\text{in}}}{y_k^{\text{in}}\left(2-\zeta_{k_{\text{prod}}}-\frac{\alpha_{k/k_{\text{prod}}}\zeta_{k_{\text{prod}}}}{1-y_{k_{\text{prod}}}^{\text{in}}\zeta_{k_{\text{prod}}}}\right)-2\left(\frac{y_{k_{\text{prod}}}^{\text{prod}}p^{\text{in}}}{p^{\text{prod}}}\right)\left(1-\alpha_{k/k_{\text{prod}}}\right)} \tag{16}$$

213 The membrane selectivities $\alpha_{k/k_{\text{prod}}}$ for the H_2 separation are obtained from Ghanbari et al.[36],

214 for the CO_2 separation from Lie et al.[45] (Table S6).

Table S6: Permeability coefficients for the H_2 and CO_2 membrane separation obtained from Ghanbari et al.[36] and Lie et al.[45], respectively.

Component	Permeability H_2 membrane	Permeability CO_2 membrane
CO	2.4	1/140
CH$_4$	2.3	1/200
CO$_2$	38	1
H$_2$	55	1/175
O$_2$	8.3	1/200
N$_2$	1.4	1/160

Chemical reactions

216 For a chemical reaction R, $\nu_{k,R}$ denotes the stoichiometric coefficient of component k. The

217 conversion rate ξ_R is determined on basis of the limiting key component k_{key}. Overall mole

balance:

$$n^{\text{in}}(1 + \sum_k \nu_{k,R}\xi_R y_{k_{\text{key}}}^{\text{in}}) = n^{\text{out}} \tag{17}$$

Component mole balance:

$$n^{\text{in}} \left(y_k^{\text{in}} - \frac{\nu_{R,k}}{\nu_{R,k_{\text{key}}}} \xi_R y_{k_{\text{key}}}^{\text{in}} \right) = n^{\text{out}} y_k^{\text{out}} \tag{18}$$

Energy balance with enthalpy of reaction ΔH_R:

$$n^{\text{in}}(h^{\text{in}} - \xi_R y_{k_{\text{key}}}^{\text{in}} \Delta H_R) + q\eta_{\text{HE}} = n^{\text{out}} h^{\text{out}} \tag{19}$$

The occurring reactions are modelled with fixed conversion rates and reaction temperatures. These parameters can be found in Table S7. However, the reaction temperature can be varied in a given range depending on the unit operations used upstream of the reactor. $\frac{n_{k_s}}{n_{k_{\text{key}}}}$ denotes the ratio of supplemented co-reactant k_s to key component in the feed stream. Concurrent to the SMR at its operating condition, the WGSR reaction takes place with $\xi_{CO}^{WGSR} = 0.4$.

Table S7: Reaction parameters of the separation system

Reaction	ΔH_R in kJ/mol	T_R in K	k_{key}	$\xi_{k_{\text{key}}}$	k_s	$\frac{n_{k_s}}{n_{k_{\text{key}}}}$
WGSR	-41.1	473 - 573	CO	0.96	H_2O	1
SMR	234.7	1153 - 1300	CH_4	0.82	H_2O	3.68
POR	-35.9	1000	CH_4	0.95	O_2	0.48
CDR	247	1143 - 1313	CH_4	0.9	CO_2	1

List of abbreviations and mathematical symbols

Abbreviation	Explanation
BFG	Blast Furnace Gas
BOFG	Basic Oxygen Furnace Gas
CCU	Carbon Capture and Utilization
CCA	Carbon Chemical Absorption
CDR	Carbon Dioxide Reforming (of Methane)
CHP	Combined Heat and Power Unit
COG	Coke Oven Gas
GDP	Generalized disjunctive (optimization) program
GHG	Green House Gas
GWI	Global Warming Impact
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LTSR	Low Temperature Shift Reaction
LP	Linear (optimization) program
MEA	Monoethanolamine
MGS	Steel Mill Off-Gas Separation
MINLP	Mixed-integer non-linear (optimization) program
MSP	Membrane Separation Process
MIP	Mixed-integer linear (optimization) program
NLP	Non-linear (optimization) program
SMR	Steam Methane Reforming
TCM	Technology Choice Model
TRL	Technology Readiness Level
TSA	Temperature Swing Adsorption
POR	Partial Oxygen Reforming (of Methane)
PSA	Pressure Swing Adsorption

Symbol	Explanation	Unit
C_p	Molar heat capacity	$\mathrm{kJ\,mol^{-1}\,K^{-1}}$
c_p	Specific heat capacity	$\mathrm{kJ\,kg^{-1}\,K^{-1}}$
ΔH_R	Reaction enthalpy	$\mathrm{kJ\,mol^{-1}}$
h	Molar enthalpy	$\mathrm{kJ\,mol^{-1}}$
M	Molar weight	$\mathrm{kg\,mol^{-1}}$
n^i	Molar flow	$\mathrm{mol\,yr^{-1}}$
p	Pressure	bar
p_k	Production volume of chemical component k	$\mathrm{Mt\,yr^{-1}}$
q	Heat flow	$\mathrm{MJ\,yr^{-1}}$
R	Gas constant	$\mathrm{kJ\,mol^{-1}\,K^{-1}}$
T	Temperature	K
t	Temperature	$^\circ C$
w	Electricity flow	$\mathrm{MJ\,yr^{-1}}$
X	Mass loading	–
y_k^i	Mole fraction (gas) with $i \in \{in, out\}$	–
α	Membrane selectivity	–
β	Adsorbent selectivity	–
η	Efficiency	–
κ	Molar heat capacity ratio	–
ν	Stoichionetric coefficient	–
ξ	Conversion rate	–
ζ^i	Split factor	–
ζ_k	Product recovery	–

Subscripts	Explanation
ads	Adsorber
des	Desorber
prod	Product component
key	Key component
k	Chemical component k

Superscripts	Explanation
i	Stream i in separation system
lean	Lean solvent stream
rich	Rich solvent stream
prod	Product stream
in	Input stream
out	Output stream

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