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Kappenthuler, Steve ; Oliveira, Sandro ; Wehrli, Jonathan ; Seeger, Stefan

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Environmental assessment of alternative methanesulfonic acid production using direct activation of methane

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ABSTRACT

In this paper we present a comparative life cycle assessment of two processes for the industrial production of methanesulfonic acid. The conventional multi-step process for the production of methanesulfonic acid is based on the reaction of methanol and hydrogen sulfide to form methanethiol which is used to produce dimethyldisulfate. The dimethyldisulfate reacts further with nitric acid to form methanesulfonic acid. A newly developed process presents the possibility to form methanesulfonic acid directly from methane and sulfur trioxide in a single step at mild conditions. Thus this process enables for the first time the production of a high value chemical through direct activation of methane on an industrial scale. The cradle-to-gate life cycle assessment conducted with the ReCiPe Method revealed that this direct process has a total environmental impact that is 3 times lower than that of the conventional process. The differences resulted from lower energy requirements and alternative reactants used in the direct process. The results therefore demonstrate the potential for methane extracted from natural gas as a greener alternative to oil as a chemical feedstock in the medium term.

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1. Introduction

Unprecedented global demand for energy and resources has led to ever increasing global temperatures and changing climates affecting billions of people around the globe. As governments worldwide attempt to slow down and mitigate the effects of climate change there is an urgent search for renewable sources for the production of fuels and chemicals. Currently these materials are almost exclusively based on petroleum, a non-renewable resource responsible for the majority of global greenhouse gas emissions. Until cost-effective technologies based on renewable sources can be used on industrial scale, natural gas could play an important role as an alternative, secure and economical carbon feedstock (McFarland, 2012). In contrast to petroleum, methane (CH_4), the main component of natural gas, exists in enormous quantities on our planet and as it can be produced from biological sources its usage as a feedstock has the potential to be much more environmentally friendly (Haynes and Gonzalez, 2014). However, currently around 3% of the annual CH_4 production is flared and about 90% is burned to create energy, which is a very low value usage of this valuable resource (Horn and Schlögl, 2015). Therefore, CH_4 's

potential as a carbon feedstock is not even close to being exhausted (Caballero and Pérez, 2013). One reason for this is the lower mass and energy density of CH_4 compared to oil, which makes the transportation and handling comparatively expensive (Horn and Schlögl, 2015). Another reason is that no economically sensible large scale process to directly produce higher value chemicals from this rather inert gas has yet been developed (Gunsalus et al., 2017). To date the majority of CH_4 used as a chemical feedstock is first converted to synthesis gas (syngas), consisting of hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2), mainly by steam reforming (Guo et al., 2014; Peplow, 2017). In a second step, the synthesis gas can be used e.g. for the production of methanol (MeOH), for the Fischer-Tropsch synthesis and for ammonia production (Nahreen et al., 2016). However, this method is not particularly energy efficient and compared to the direct conversion of CH_4 it is seen as potentially less economical and less environmental friendly (Haynes and Gonzalez, 2014; Schwach et al., 2017).

Recently the direct conversion of CH_4 to methanesulfonic acid (MSA) under mild conditions was reported (McCoy, 2016). In the presence of sulfur trioxide (SO_3) CH_4 can be converted at low temperatures and moderate pressure to a high-value added chemical with high yield (Ott and Biertümpel, 2017). A big advantage of the reaction is that to the best of our knowledge, for the first time, CH_4 can be converted in only one reaction step to a high-value chemical on an industrial scale. At present MSA is mainly produced

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Nomenclature

CH ₄	methane
CH ₃ SH	methanethiol
CO	carbon monoxide
CO ₂	carbon dioxide
DMDS	dimethyldisulfide
EI	environmental impact
EIP	environmental impact points
FU	functional unit
H ₂	hydrogen
HNO ₃	nitric acid

H ₂ O ₂	hydrogen peroxide
H ₂ S	hydrogen sulfide
H ₂ SO ₄	sulfuric acid
LCA	life cycle assessment
LCI	life cycle inventory
MeOH	methanol
MSA	methanesulfonic acid
NO ₂	nitrous oxide
NO _x	nitrogen oxide pollutants
SO ₂	sulfur dioxide
SO ₃	sulfur trioxide
Syngas	synthesis gas

via the conversion of syngas to MeOH which undergoes further reactions with hydrogen sulfide (H₂S) and nitric acid (HNO₃) (McCoy, 2016). Compared to this conventional route of MSA production it is likely that the direct conversion of CH₄ to MSA will decrease the production costs due to reduction of process complexity. MSA presents an environmentally friendly alternative to different acids since it is a strong but non-oxidizing and non-corrosive acid which is biodegradable, and forms salts that are highly soluble and also non-hazardous (BASF SE, 2011; Gernon, 1999). For instance MSA can be used instead of phosphoric acid in the formulation of cleaning agents since it contains no phosphorous and therefore does not contribute to eutrophication and the associated increase in algal growth (BASF SE, 2011). It has also been used to replace hazardous fluoroboric acid as the main electrolyte in the industrial electroplating of zinc and lead (Gernon, 1999). A decrease of production costs could open up additional application fields enabling further substitution of conventional acids with this *green* acid. Additionally as mentioned, the direct one-step production of MSA promises to be more environmentally friendly than the indirect production process via syngas, consequently further increasing the sustainability of this product (Schwach et al., 2017). In order to fully understand and quantify this potential improvement in process sustainability we present for the first time a comparative life cycle assessment (LCA) of the two production processes; one based on the direct CH₄ conversion and one based on the indirect conversion of syngas to MeOH. This includes a detailed description of the individual industrial processes.

2. Data and methodology

2.1. System boundaries and goal of LCA

An LCA assesses the environmental impact (EI) of products and processes of their entire life cycles (cradle-to-grave). This includes all activities from acquisition and processing of raw materials, production and distribution of the product itself including its use, reuse, maintenance and disposal. In this case, for the comparison of the environmental impact of two different methods for the production of an identical product (i.e. MSA) a cradle-to-gate process is sufficient since the use and disposal steps are assumed to be identical for both processes. Therefore the system boundaries only include the acquisition and processing of raw materials up to the final MSA product. For both processes transportation of raw materials to the factory as well as the impacts from producing the factory infrastructure are not included. Catalysts are also not included as they can be reused and thus have little impact on the overall results when compared to the main reactants. Some of the reactions involved in MSA production are exothermic and release energy which can be directly used as heat or converted to

electricity. As industrial chemical production is designed to maximize efficiency through a production network these energies were subtracted from the overall energy required in both cases. Finally for both processes the energy requirements of auxiliary components (e.g. pumps used between the single reaction steps, compressors, measuring devices, etc.) were not included since proper data could not be realistically estimated. With regard to the comparison of the two production processes, these exclusions are favorable for the conventional process since it requires more starting material for transport and consists of more reaction steps.

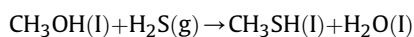
The goal of this LCA is to compare the amount and sources of the EIs of the two MSA production processes shown in Fig. 1. Both processes as well as the assumptions and calculations surrounding the life cycle inventories are discussed in more detail in sections 2.3 and 2.4. For the individual LCA calculations SimaPro LCA software was used which is based on the ecoinvent 3.3 database. In order to compare the full EIs of both processes as well as the individual sources of the impacts the results were computed in the form of the ReCiPe 1.13 End- and Midpoint (Hierarchist) categories.

2.2. Functional unit

The functional unit (FU) must provide a reference to which all input and output numbers within the LCA can be related. Since this LCA focuses on the comparison of two production processes of MSA the FU was defined as 1000 kg of 99.5% pure MSA produced. The environmental impacts are all presented in reference to the FU, e.g. carbon dioxide emission will be referenced and compared as kg CO₂ produced per 1000 kg of pure MSA.

2.3. Conventional process

The conventional process for producing MSA which is presented here is used to produce around 30'000 tons of MSA a year which represents the majority of global MSA production volume (BASF SE, 2012). The basic raw material inputs into the process are sulfur from petroleum refinery for the production of H₂S and natural gas for the production of MeOH via the syngas pathway. In a first step excess H₂S reacts with MeOH (3:2 M ratio) to form methanethiol (CH₃SH) by using a potassium tungstate and aluminum oxide catalyst with a 98% yield (Woelfert et al, 2008a, 2008b, 2008c, 2010).



CH₃SH reacts further with pure sulfur and a secondary amine as the main catalyst. The reaction products are dimethyl disulfide (DMDS; CH₃S–S–CH₃) and H₂S which can be reused for the first reaction. Excess H₂S is burned in a Claus process used for gas

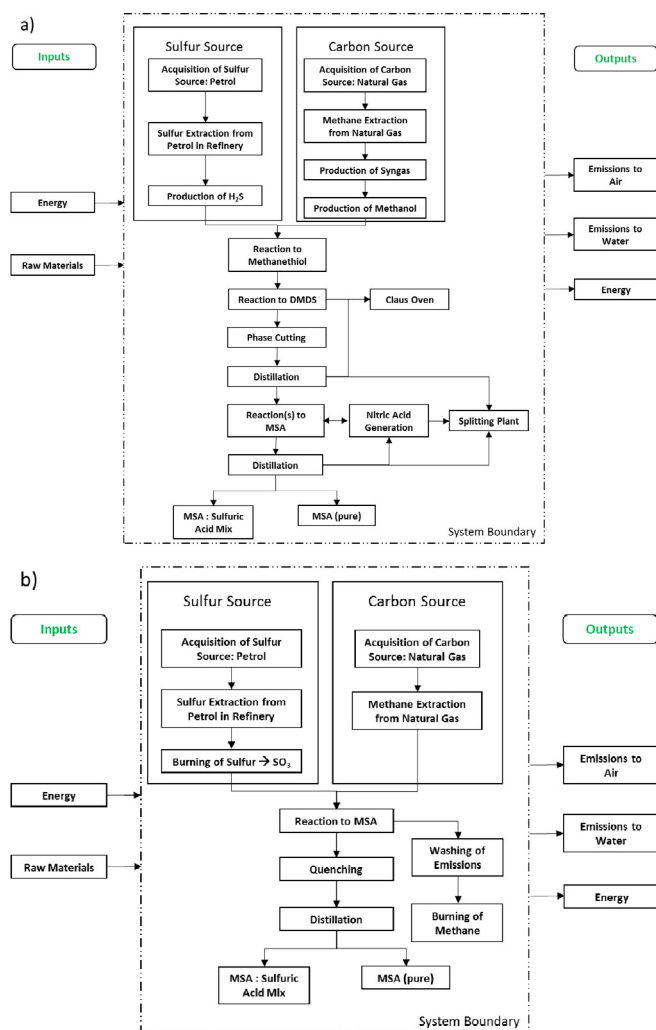
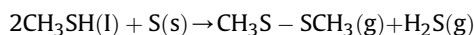
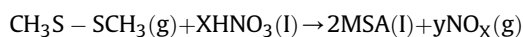


Fig. 1. Description and system boundaries for LCA of a) conventional and b) direct MSA production process.

desulfurization to produce pure sulfur which can in turn be reused for the DMDS reaction. The yield based on industry estimates and patent data is 90% with polysulfides ($\text{CH}_3\text{S}_x\text{CH}_3$) as a waste product (Gunnar et al., 2002; Hesse et al., 2000).



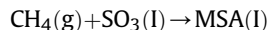
The DMDS is brought into a first reactor where it reacts with excess amounts of HNO_3 to form MSA (1:5 M ratio). Nitrogen oxide (NO_x) byproducts flow into a nitric acid generation column to regain HNO_3 for further reactions while the other products and byproducts are sent to two vacuum columns in turn. This leads to some of the MSA to react to sulfuric acid (H_2SO_4) and MSA-methyl esters. H_2SO_4 is mixed with part of the MSA and can be seen as a byproduct while the esters are usually treated as waste. The yield of the MSA reactions and distillations is estimated at 93% (Eiermann et al., 2000; Fassbender et al., 2011).



For the life cycle inventory (LCI) (See Appendix B) the data for the quantity of educts and products and reaction yields was gathered from the production process patents as well as from experts involved in MSA production.

2.4. Direct process

The direct process utilizes CH_4 and SO_3 in H_2SO_4 to create MSA in a one-step reaction (Ott and Biertümpel, 2017; Ott et al., 2015).



Hydrogen peroxide (H_2O_2) is added to the reaction to create an activating agent which accelerates the reaction with yields of 95%. The activator has the formula $\text{Alk}-\text{SO}_2-\text{O}-\text{O}-\text{SO}_2-\text{OX}$ (Alk: methyl, ethyl, propyl, butyl, isopropyl, isobutyl group, or a higher alkyl group; X: hydrogen, zinc, aluminum, an alkali or alkaline earth metal). Excess SO_3 is treated with water to create H_2SO_4 . Non reacting MeOH is flared. After the distillation the products are MSA (99.5% pure) and a H_2SO_4 , MSA mixture with an 80:20 ratio.

Data for the LCI (See Appendix B) regarding raw material quantities and origin as well as the respective reaction yields were gathered through patents and industry estimates. For the amounts of sulfur being used the data were collected from information on the double contact process that forms the starting material SO_3 . Information was gathered from industry sources and compared with literature (European Commission, 2007).

The conversion rate from natural gas to pure CH_4 was calculated by using data on pressure swing adsorption for the purification process (Wu et al., 2015).

For both processes the raw sulfur source was sulfur gained from European petroleum refineries found in the ecoinvent database. Both processes also share the same carbon source which is natural gas, mined in Norway, from the ecoinvent database.

2.5. Collection & estimation of emissions data

For the conventional process the amount of direct CO_2 and sulfur dioxide (SO_2) emissions formed during MSA production were calculated directly from the waste/emission data of the amounts suggested by patents and industry estimates. For the Claus process, emission data was gathered from publications and scaled to the FU (Jacobs Comprimo Sulfur Solutions; Manenti et al., 2013; Sassi and Gupta, 2008). It was assumed that the Claus process was at the highest efficiency with SO_2 emissions of 0.2% per ton sulfur produced. The same assumptions were made for SO_2 emissions by the splitting plant. The treatment of NO_x from the nitric acid generation plant was considered to be emission free. Emissions from nitric acid generation was taken from the ecoinvent database and adjusted with data from literature (Kamphus, 2014) since the emissions data was quite old and no longer reliable.

The estimates for the emissions caused by the direct process were gathered from industry sources. CO_2 emissions were calculated directly from the amounts of non-reacting CH_4 that is estimated to flow into the waste treatment.

Emissions from the production of raw materials of both processes was taken directly from the ecoinvent database. Indirect emissions from energy consumption were calculated with SimaPro using German electricity at medium voltage and thermal heat generated from natural gas.

2.6. Collection & estimation of energy data

Most of the energy used in both processes was chosen in the form of thermal energy from natural gas and electricity at medium voltage produced in Germany in a 90:10 ratio.

Energy data for the conventional process was estimated and calculated using patent information, industry estimates and literature. The reaction energies were calculated using thermodynamic data following an estimation method developed by Piccinno et al.

(2016). For the DMDS reaction the mentioned method could not be applied due to the complex mechanism, so industry estimates and patent information was used instead (Gunnar et al., 2002; Hesse et al., 2000). For the nitric acid generation column the energy estimate was based on a study by Anastasopoulou et al. (2016).

Since factories for the direct process are not yet built, the publishers of the patent were contacted for information on energy requirements. A list of energy calculations for MSA production (step 3 Appendix A2) was received and used for the LCI. Energy generation and requirements from SO₃ production were calculated with the information received from industry sources.

Energy required for H₂S, MeOH and HNO₃ production was taken directly from ecoinvent. The energy required for the distillations was estimated with the help of industry experts involved in the production of MSA. Energy required for sulfur and natural gas production for both processes were taken directly from the database.

For a detailed description of all individual production steps see Appendix A.

3. Results & discussion

3.1. LCA results of entire processes

The ReCiPe Endpoint results provide a high level comparison of the overall cradle-to-gate impacts of the production of 1000 kg of 99.5% pure MSA for both production processes. As shown in Fig. 2 the overall environmental impact of the conventional process (209.5 Environmental Impact Points (EIP)) is 3 times higher than that of the direct process (70.1 EIP) thus making the direct process more sustainable.

The midpoint results give the same picture with reductions from the conventional to the direct process ranging from 46 to 94% as shown in Table 1. It is noteworthy that the direct process has a lower score for every single midpoint category. In order to determine which type of impact contributes most to each process' overall impact, the impact categories which combine to the total endpoint EI were analyzed. As can be seen in Fig. 3, the same four impact categories account for over 95% of the final score for both processes. Fossil depletion stemming from the use of fossil fuels such as petroleum, natural gas and coal for the production of energy and input materials make up the largest share for both

processes being responsible for 57.8% of all EI of the conventional and 71.6% of the direct one. This is followed by emissions of greenhouse gases leading to climate change measured in CO₂ equivalents. The formation of particulate matter is the smallest of the four major impact categories accounting for 3.1 and 3.8% of total impact of the conventional and direct processes respectively. For an overview of all 17 impact categories see Appendix C.

3.2. Comparison of impact sources

For a more detailed analysis of the sources of these large differences between the two processes the impacts of the different inputs and outputs were calculated. In order to be able to better compare the two very different processes the inputs were grouped into carbon, sulfur and oxygen source/other chemicals, as well as electrical and thermal energy (required as input during the production process, excluding the production of the carbon, sulfur and oxygen sources). All outputs arising from the transformation of the different sources to MSA were treated as direct emissions. Both processes still produce water and air. Since these do not have any environmental impact they were not included in the comparison. Table 2 shows the detailed composition of all the inputs and outputs for both processes which are also labeled in Fig. 1. Fig. 4 shows the impacts of the different inputs and outputs as well as the differences for each between the two MSA production processes.

Electrical & thermal energy contributes to 34% of the total EI of the conventional process and 20% of the direct one. Greenhouse gases and other pollutants emitted through the generation of electricity by mining and burning coal as well as the depletion of fossil fuels (petroleum, coal and natural gas) are the main impact sources. The conventional process requires multiple reaction steps and multiple distillations, while the direct process is a one step process with a single distillation. Therefore it is to be expected that more energy is needed for the conventional process, hence producing a higher impact. Even though the input of energy accounts for the largest difference between the two products the choice of reactants also has a major influence on the improved sustainability of the direct process.

The impact of the carbon source is much higher for the conventional process due to the use of MeOH as reactant which is produced via the syngas route. Energy is required to extract CH₄ from the natural gas source, then to produce syngas from the CH₄

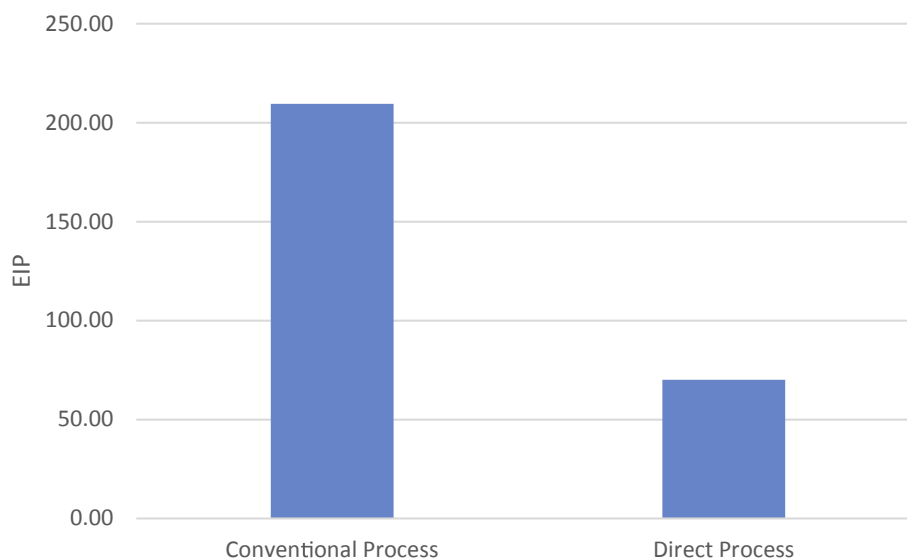
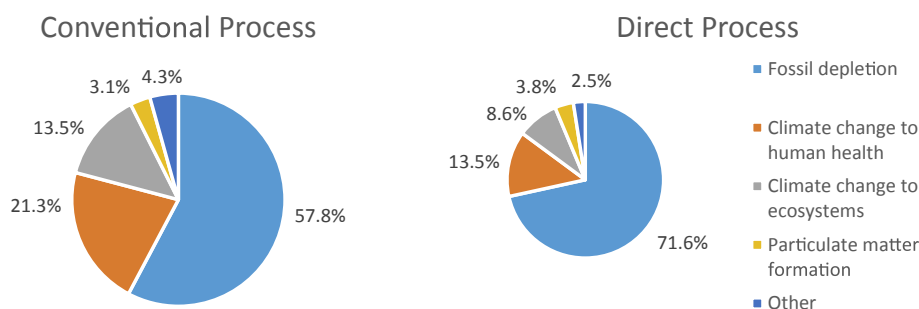


Fig. 2. Comparison of total environmental impact of MSA production.

Table 1

Comparison of Midpoint results for MSA production processes in order of contribution to overall impact.

Midpoint	Unit	Conventional	Direct	% Reduction
Fossil depletion	kg oil eq	1129.6	468.6	58.4%
Climate change	kg CO ₂ eq	1613.2	246.4	84.7%
Particulate matter formation	kg PM ₁₀ eq	1.2	0.52	57.8%
Natural land transformation	m ²	0.85	0.40	52.5%
Metal depletion	kg Fe eq	31.9	5.0	84.4%
Human toxicity	kg 1,4-DCB ^a eq	348.5	33.4	90.4%
Urban land occupation	m ² * yr	3.6	0.84	76.3%
Agricultural land occupation	m ² * yr	34.4	2.2	93.5%
Terrestrial acidification	kg SO ₂ eq	3.9	2.1	46.0%
Terrestrial ecotoxicity	kg 1,4-DCB eq	0.045	0.012	73.2%
Freshwater ecotoxicity	kg 1,4-DCB eq	9.7	1.3	86.6%
Freshwater eutrophication	kg P eq	0.45	0.040	91.2%
Ozone depletion	kg CFC-11 ^b eq	3.3E-04	1.6E-04	51.7%
Ionising radiation	kBq U ²³⁵ eq	129.8	36.5	71.9%
Photochemical oxidant formation	kg NMVOC ^c	2.9	0.83	70.9%
Marine ecotoxicity	kg 1,4-DCB eq	10.1	1.5	85.0%
Marine eutrophication	kg N eq	0.22	0.024	88.5%
Water depletion	m ³	15.1	4.3	71.6%

^a 1,4-DCB: 1,4 dichlorobenzene.^b CFC-11: Chlorofluorocarbon.^c NMVOC: Non Methane Volatile Organic Carbon compound.**Fig. 3.** Contribution of impact categories to total EI of MSA production.**Table 2**

Composition of inputs/outputs of MSA production processes.

Input/Output	Conventional Process	Direct Process
Carbon source	MeOH	CH ₄
Sulfur source	H ₂ S, S	SO ₃
Oxygen source/other chemicals	HNO ₃	SO ₃ , H ₂ O ₂
Electrical & thermal energy	Electricity Mix DE, Natural Gas Furnace	Electricity Mix DE, Natural Gas Furnace
Direct emissions	CO ₂ , SO ₂	CO ₂

and then finally MeOH. The overall yield of MeOH formation from syngas for the conventional process is only around 90% (Ecoinvent database). Thus more natural gas resources as well as additional production energy are required per ton of MSA produced. The direct process on the other hand simply uses CH₄ as a carbon source after extraction from natural gas. Nevertheless the mining, pipeline-transportation and CH₄ extraction of natural gas has a significant EI and accounts for almost 35% of the entire process.

The sulfur sources also show a significant difference because H₂S is required in the conventional process while the direct process uses SO₃. Beside sulfur, H₂S production requires H₂ as a further input. This needs to be obtained through steam reforming or other industrial processes and has to be compressed for transportation before use, thus leading to additional emissions and fossil depletion due to the energy required. While SO₃ production does account for 38% of the direct process' total EI it is still a more environmentally friendly sulfur source than H₂S. Firstly, the production of SO₃ only requires air as an additional reactant which causes no additional

environmental impact. Secondly the burning of sulfur and SO₂ is an extremely exothermic reaction. The resulting electrical energy (generated through steam turbines) can be subtracted from the input into SO₃ production as it avoids or compensates the use of other energy sources. It would also have been possible to subtract this energy from the thermal and electrical energy required for the overall MSA production. However since the formation of SO₃ is not directly part of the MSA synthesis this allocation was used. The overall environmental impact score is not affected by this choice.

Concerning the oxygen source the direct process performs better as well. SO₃, which is already the sulfur source, is also the main oxygen source and cannot be counted twice. This leaves very small amounts of H₂O₂ as additional chemicals which are used to produce an activator (Alk-SO₂-O-O-SO₂-OX) for the MSA reaction. The conventional method on the other hand requires a constant input of HNO₃ as the main oxygen source. While most of the HNO₃ can be retrieved in the form of NO_x and reformed using air and water for further use, certain emissions are unavoidable. This

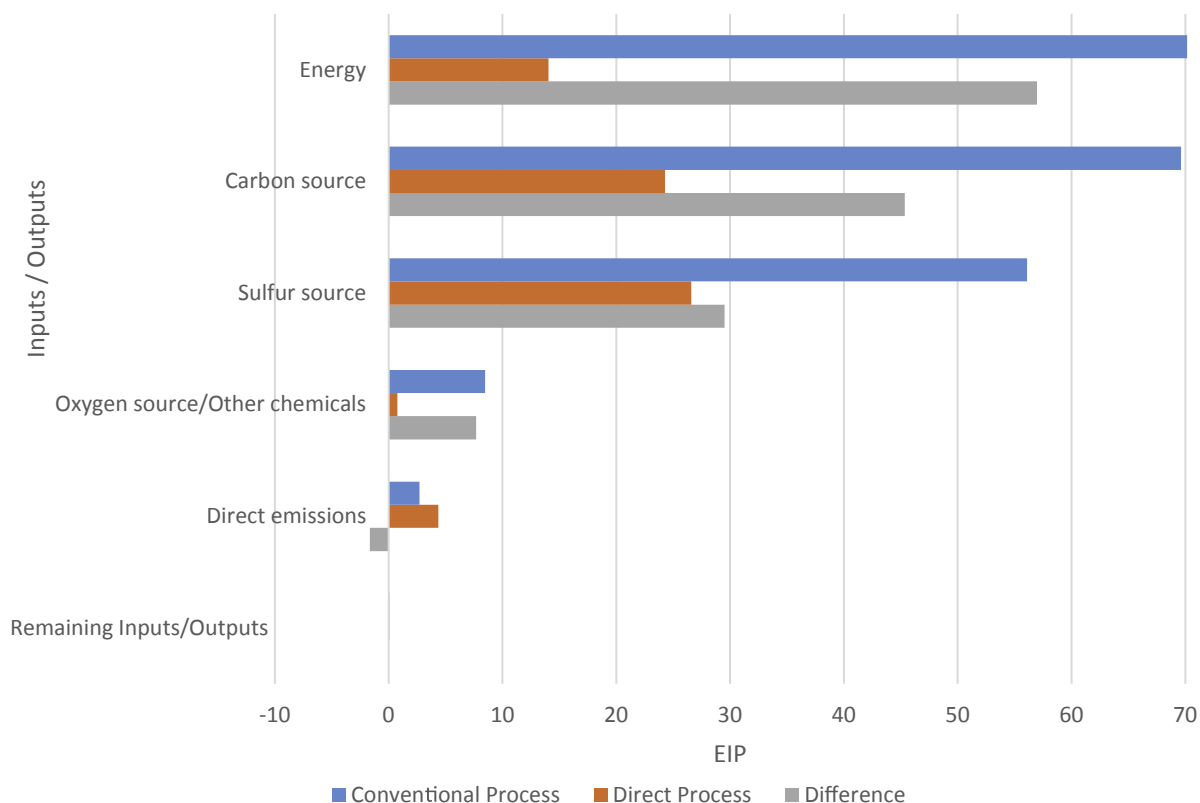


Fig. 4. Comparison of EI of inputs and outputs of MSA production processes.

means that new HNO_3 steadily needs to be added to the recycled amounts. The exhaust air arising from this recycling process is assumed to be treated very effectively with no nitrogenous substances entering the atmosphere. Nevertheless the production of new HNO_3 from ammonia requires both extra energy and produces the most nitrous oxide (N_2O) across the entire LCA at 177.2 g/FU (compared to 195.4 g/FU for the entire conventional process and 2.97 g/FU for the direct process).

The emissions considered in this comparison are only the direct emissions of the production processes and do not include indirect emissions from power generation or production of the reactants. For the direct process these are mainly CO_2 emissions from the burning of excess CH_4 . The conventional method produces CO_2 in smaller quantities in a splitting plant together with small amounts of SO_2 . Additional SO_2 is produced and enters the atmosphere during the recovery of sulfur from the burning of H_2S exhaust gas. As shown in Fig. 5, the direct process (94 kg CO_2 eq/FU) has higher direct emissions than the conventional one (50 kg CO_2 eq/FU). This is solely due to the fact that excess CH_4 is flared in the direct process, while the conventional processes is extremely efficient, containing multiple recycling steps, therefore minimizing the production of waste. The direct process could therefore be further improved if the unreacted CH_4 were reintroduced into the reactor for MSA production or at least utilized to produce energy. Despite this inefficiency, if one considers the total indirect emissions arising throughout the entire value chain this difference in direct emission becomes negligible. The conventional process produces 1425 kg CO_2 eq/FU of indirect emissions mainly due to the production of the input materials and energy, while the direct process only emits 234 kg CO_2 eq/FU. That is a difference of 1191 kg CO_2 eq/FU which dwarves the difference of direct emissions of 44 kg CO_2 eq/FU as illustrated in Fig. 5.

Overall the reasons why the direct process is more

environmentally friendly are pretty straight forward. The direct method for MSA synthesis has fewer reaction and purification steps and therefore requires less energy thus producing fewer indirect emissions and impacts. Furthermore the substances used as starting reactants are not only more environmentally friendly themselves but are also used in smaller quantities. For instance CH_4 is further up the value chain than MeOH and doesn't require extra production steps. SO_3 produces energy as a byproduct and only requires air and sulfur for production compared to sulfur and H_2 required for H_2S . Finally SO_3 also acts as an oxygen source while HNO_3 is required in the conventional process which again requires energy and produces significant amounts of N_2O .

4. Conclusion

To the best of our knowledge this paper presents the first quantitative analysis of the improvement in sustainability that can be achieved through the direct activation of methane in an industrial chemical process. The comparative LCA between the conventional production process of MSA and the newly developed, direct process shows that the direct process has an EI that is 3 times lower than the conventional one. GHG emissions are reduced by 85% while fossil depletion is reduced by 58%. Furthermore every single midpoint category is reduced by at least 46% when evaluated using the ReCiPe Method. The main reason for these reductions is that the possibility of activating CH_4 enables a one-step reaction for the formation of MSA, which significantly reduces the complexity of the process. The conventional route first requires the production of syngas and MeOH as well as multiple further reactions all of which require energy and thus produce a large amount of indirect emissions and environmental impacts. A further advantage of the direct process is the use of reactants which are further up the value chain again requiring less energy. Due to a lack of reliable data the

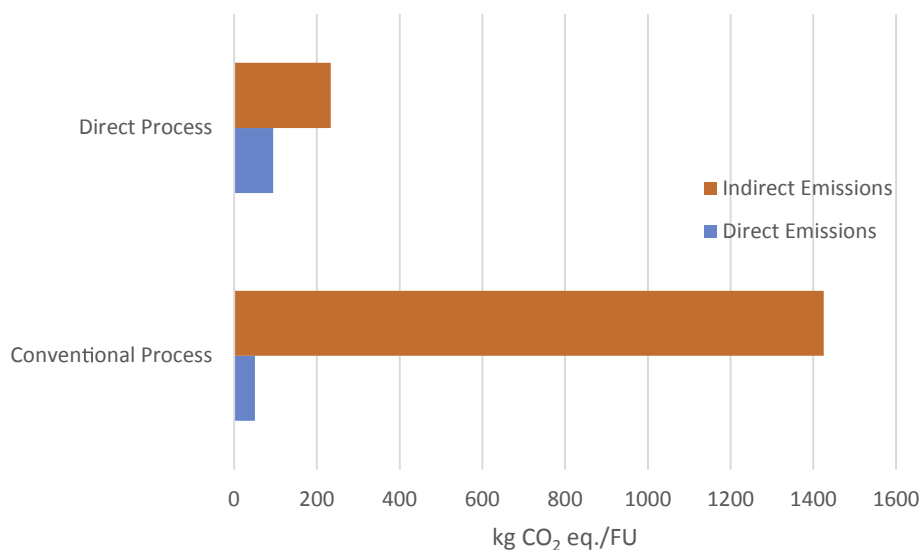


Fig. 5. Comparison of direct emissions (arising from individual production steps) and indirect emissions (arising from production of input materials and generation of energy required for individual production steps) for MSA production processes.

presented results do not include energy requirements of auxiliary process equipment which could increase the absolute EI values for both processes. As the conventional process consists of more individual production steps and thus requires more auxiliary equipment, an inclusion of this factor would further increase the difference in EI of the two analyzed processes.

While the direct activation is definitely a step towards the use of CH₄ instead of petroleum as a feedstock for the production of higher value chemicals it may not be ignored that the extraction of natural gas also produces significant environmental impacts and it cannot be considered as a renewable or long term sustainable resource. Therefore future work should investigate possibilities to further increase the sustainability of MSA production. The production of CH₄ from biological waste could be a promising option as this would introduce a truly renewable resource into the process. Furthermore it would be interesting to analyze the possibility of

supplying the entire process with energy from renewable sources.

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Declarations of interests

None.

Appendix A. Stepwise process description

A1. Conventional process

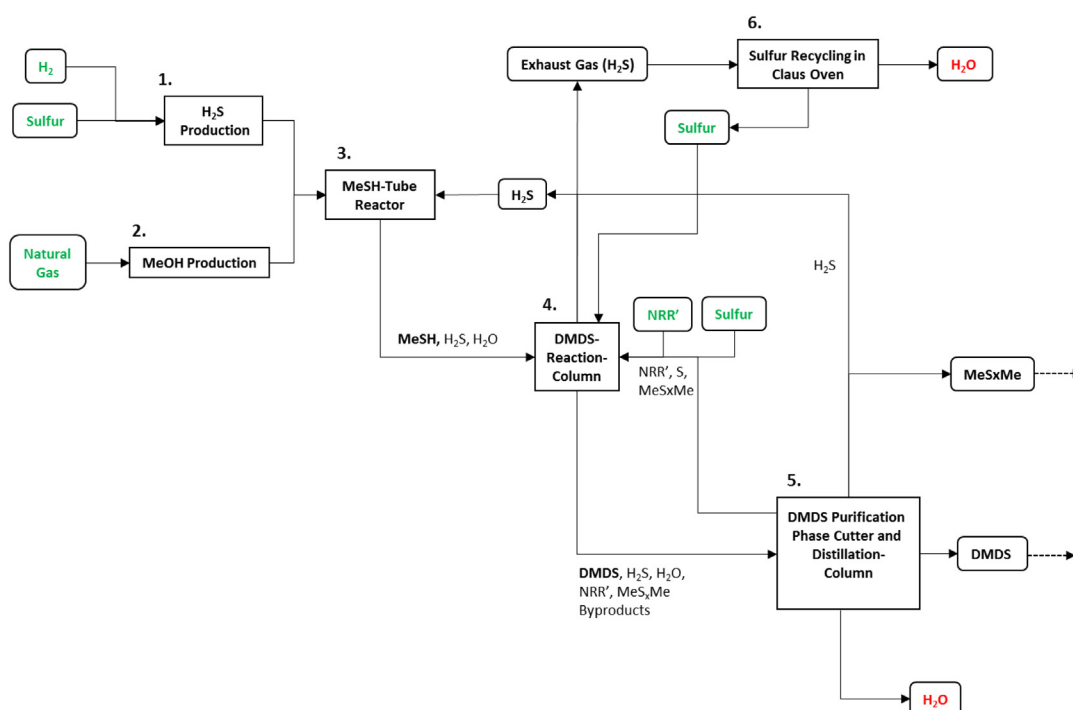


Fig. A.1. Stepwise overview of conventional process (1/2).

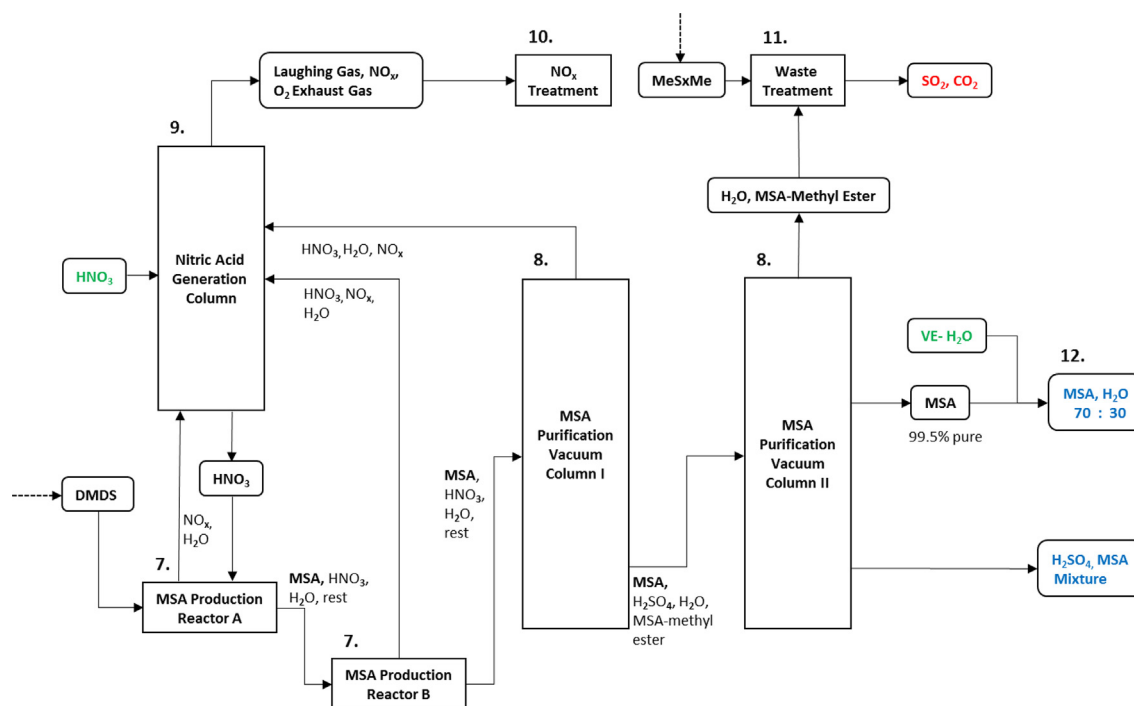


Fig. A.2. Stepwise overview of conventional process (2/2).

1 H₂S Production:

Data for production was taken directly from the Ecoinvent database and compared to patent data (Woelfert et al., 2008a, 2008b, 2008c, 2010). The yields found in the patents were considerably higher than those given in Ecoinvent. Therefore the Ecoinvent data was adjusted to reflect modern production processes. Data on sulfur and hydrogen production was taken from Ecoinvent.

Energy required: 104 kWh
Inputs: 352 kg S/22 kg H₂
Output: 370 kg H₂S

2 MeOH Production:

Natural gas from Norway is formed to syngas and finally to methanol. All data was taken from Ecoinvent.

Energy required: 1039 kWh
Inputs: 344 m³ natural gas
Output: 527 kg CH₃OH

3 MeSH Production:

Hydrogen sulfide is compressed and led into a reactor together with methanol. It reacts at 350–450 °C and 1.1 bar to form methanethiol at 98% yield (Brand, 2003; Brand and Quasching, 2004). The energy was calculated according to Piccinno et al. (2016). It was assumed that a 110 m³ reactor is used at a temperature of 400 °C and a reaction time of 1 h.

Energy required: 135 kWh

Inputs: 370 kg H₂S (new)/452 kg H₂S (led back from later steps)/527 kg CH₃OH
Output: 758 kg CH₃SH/579 kg H₂S intermediate and other byproducts

4 DMDS Production:

Methanethiol is added to a reaction column at 40–60 °C and standard pressure. Sulfur is added together with a secondary amine at 70–100 °C as the main catalyst (Gunnar et al., 2002). The reaction products are DMDS and hydrogen sulfide which is led back to the previous reaction or burned in a Claus process to produce sulfur for recycling. 90% of the polysulfides which are produced as a byproduct are led back into the DMDS reaction after purification, while 10% are assumed to be treated as waste together with the other byproducts (Gunnar et al., 2002; Hesse et al., 2000). The reaction yield and energy required for the entire process was based on estimates of industry experts.

Energy required: 500 kWh
Inputs: 758 kg CH₃SH/579 kg H₂S intermediate and other byproducts/200 kg Sulfur (69.41 kg new and rest recycled)/325 kg polysulfides from purification
Outputs: 527 kg DMDS/452 kg H₂S (led back to previous reaction)/200 kg H₂S (70%) (led to Claus Oven)/362 kg polysulfides/290 kg H₂O/60 kg other byproducts

5 DMDS Purification (phase cutter & distillation column):

All the outputs of the DMDS reaction (except hydrogen sulfide) are led into a phase cutter at 90 °C and 1 bar where the water is separated from the other intermediates. The other substances are

led into a distillation column estimated to be operating at 65 °C and 300 mbar (Hesse et al., 2000). The energy consumption was based on the values for the distillation in step 4 of the direct process.

Energy required: 100 kWh

6 Sulfur Recycling (Claus Process):

Some of the excess hydrogen sulfide of the DMDS reaction is burned to recover sulfur which is reused for the DMDS reaction. Yield, energy requirements and emissions were calculated with data from literature (Jacobs Comprimo Sulfur Solutions; Manenti et al., 2013; Sassi and Gupta, 2008).

Energy required: 2 kWh

Inputs: 200 kg H₂S (70%)

Outputs: 132 kg Sulfur (led to DMDS production)

Emissions to air: 0.273 kg SO₂, 0.0001 kg NO_x, 0.0001 kg CO

7 MSA Production (Reactor A&B):

DMDS is brought into a first reactor A at 80–120 °C and standard pressure where it reacts with excessive amounts of nitric acid from a nitric acid generation column) to form MSA (1:5 M ratio). The products and additional byproducts and educts are sent to a second reactor B at 130–150 °C where it can react further and additional MSA is produced. Exhaust gas from both reactors (A: NO_x, H₂O; B: NO_x, HNO₃, H₂O) are led back into the nitric acid generation column. The other reaction products (MSA, HNO₃, H₂O, rest) from reactor B are led into a vacuum column. The yield of the overall reaction is given at 93% (Fassbender et al., 2011; Eiermann et al., 2000). The energy required for both reaction columns was calculated according to Piccinno et al. (2016). It was assumed that two separate 5.5 m³ reactors were used with a reaction time of 2 h each.

Energy required: 870 kWh (Reactor A) and 120 kWh (Reactor B).

Inputs: 527 kg DMDS/3525 kg HNO₃

Output: 1003 kg MSA/ca. 2400 kg exhaust gas/ca. 620 kg HNO₃, H₂O and other byproducts

8 MSA Purification (Vacuum Column I & II):

The products and byproducts from the MSA production are led into a first vacuum column I at temperatures of 180–190 °C and 95–100 mbar. Here nitric acid, water and nitric oxides (which are formed in the column) are separated from the other products and byproducts. Small amounts of sulfuric acid and MSA-methylesters are formed in the column and led to a second vacuum column II together with the MSA product and trace amounts of water. The vacuum column II runs at 180–190 °C and 5–10 mbar and separates the 99.5% pure MSA product, the byproduct mixture of MSA and sulfuric acid (20:80 wt ratio) and the MSA methyl esters which are treated as waste and led to a splitting plant (Fassbender et al., 2011; Eiermann et al., 2000). Since both distillations are similar to the distillation in step 4 of the direct process it was assumed that the required energy would be similar. Energy data for this step was obtained from industrial sources.

Energy required: 350 kWh (column I) and 400 kWh (column II)

Inputs: 1003 kg MSA/ca. 620 kg HNO₃, H₂O and other byproducts

Outputs: 1000 kg pure MSA (99.5%)/37.5 kg H₂SO₄ -MSA-mix (80: 20)/37.5 kg MSA-methylesters (to splitting plant)/ca. 600 kg NO_x, HNO₃ and H₂O (to nitric acid generation column)

9 Nitric Acid Generation Column:

NO_x exhaust gas, excess nitric acid and water from the MSA production and purification are led into a nitric acid generation column where additional water and air is added to form nitric acid. The nitric acid is the led back into the MSA reactor A. Exhaust gas containing NO_x is led to NO_x-treatment. Based on industrial sources it is assumed that 2.5% of the nitric acid has to be refilled by new nitric acid. Emission data had to be altered to reflect modern production processes with higher emission reduction (Kamphus, 2014). The required energy for the nitric acid generation plant was based on literature (Anastasopoulou et al., 2016).

Energy required: 450 kWh

Inputs: 88 kg new HNO₃/ca. 3000 kg NO_x, HNO₃ and H₂O;

Output: 3525 kg HNO₃ (led back to MSA production)/exhaust gas with 50 kg NO_x (led back to NO_x treatment)

10 NO_x-Treatment:

The treatment of NO_x in the exhaust gas from the nitric acid generation plant was considered to be emission free due to the strong emission regulations. Energy requirements for the filtration are low and can therefore be neglected for the overall process.

11 Waste Treatment (Splitting Plant):

The excess polysulfides from the DMDS purification and the MSA-methylesters from the MSA purification are assumed to be burned in a splitting plant which creates CO₂ and SO₂ emissions. The amount of CO₂ emissions formed in the splitting plant were calculated stoichiometrically from the substances burned in the plant. It was assumed (due to regulations) that 99.8% of SO₂ generated could be filtered so that only 0.2% would be emitted. The splitting plant was estimated to require similar amounts of energy that it would produce from the waste burned. Deviations from this zero sum total would have minimal impact on the overall results, since the waste generated and energy created is rather small and can therefore be ignored.

Inputs: 36 kg polysulfides/38 kg MSA-methylesters

Emissions to air: 50 kg CO₂/0.16 kg SO₂

12 As a final step purified water is added to the MSA product to receive a 70% aq. solution.

Input: 1000 kg pure MSA (99.5%)/414 kg water

Final Product: 1414 kg MSA_{aq} (70%)

A2. Direct process

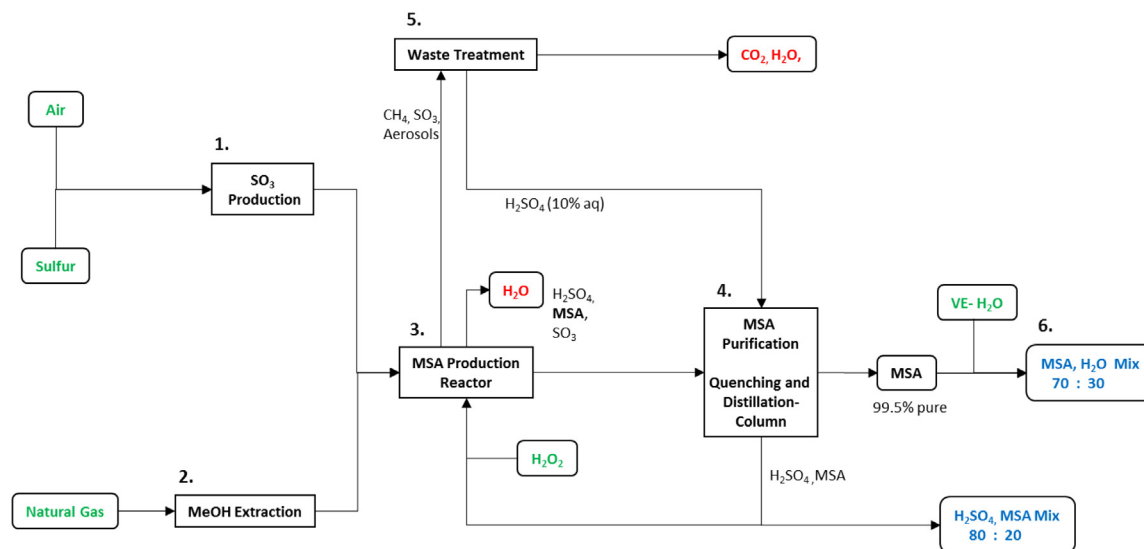


Fig. A.3. Stepwise overview of direct process.

1 SO₃ Production:

Data concerning sulfur trioxide production via the double contact method was obtained from industrial sources and compared to literature (European Commission, 2007). Data for sulfur production was taken from Ecoinvent.

Energy produced: 60 kWh
 Inputs: 385 kg S
 Outputs: 960 kg SO₃
 Emissions to air: 1.22 kg SO₂/0.021 kg SO₃

2 CH₄ Extraction:

Methane is extracted from natural gas (produced in Norway, data from Ecoinvent) using Pressure Swing adsorption. The energy required for this process was considered to be negligible (Wu et al., 2015).

Input: 408 m³ natural gas.
 Outputs: 206 kg CH₄

3 MSA Production:

Sulfur trioxide and methane react in sulfuric acid at 50 °C and 83–100 bar to form MSA. The yield and energy requirements were based on patents and industry estimates (Ott and Biertümpel, 2017; Ott et al., 2015).

Energy requirement: 159 kWh
 Inputs: 960 kg SO₃/206 kg CH₄
 Outputs: 1030 kg MSA/34 kg CH₄ (to waste treatment)
 114 kg SO₃ (to purification; partly via waste treatment)

4 MSA Purification (Quenching and Distillation):

Non-reacted sulfur trioxide from the reaction is treated with

water and reacted to sulfuric acid. The MSA, sulfuric acid and left-over water is added to a distillation column; based on physical properties (boiling point) the conditions are assumed at 200 °C and 10 mbar. Pure MSA (99.5%) is received through this distillation, as well as an 80: 20 mixture of sulfuric acid and MSA as a byproduct. Some excess sulfuric acid mixed with MSA is led back to the reactor. The yield and energy requirements for the overall purification were based on patent data and assumptions of industry experts with similar purification systems (Ott and Biertümpel, 2017; Ott et al., 2015).

Energy requirement: 413 kWh
 Inputs: 1030 kg MSA/114 kg SO₃
 Outputs: 1000 kg pure MSA (99.5%)/175 kg H₂SO₄ -MSA-mix (80: 20)

5 Waste Treatment:

Excess sulfur trioxide and methane as well as trace amounts of aerosols from the MSA production reaction is led to a washer. SO₃ is separated and reacted to sulfuric acid (10% aq.) which is added to the quenching step. Excess methane is flared. The resulting emissions were calculated stoichiometrically.

Inputs: 34 kg CH₄/SO₃
 Outputs: H₂SO₄ (10% aq.) (led back to purification)

6 As a final step purified water is added to the MSA product to receive a 70% aq. solution.

Inputs: 1000 kg pure MSA (99.5%)/414 kg water.
 Final Product: 1414 kg MSA_{aq} (70%)

Appendix B. Life cycle inventory data

Materials/Energy: Conventional Process		Kg/FU	kWh/FU
Water	Water (pure)	414.14	
Reaction Materials & Intermediates	H ₂ S	369.89	
	MeOH	515.18	
	MeSH	758.10	
	Sulfur (DMDS formation)	200.00	
	DMDS	526.95	
	Dicyclohexylamine	1.48	
Products/Byproducts	HNO ₃	88.12	
	MSA (diluted 70%)	1'414.15	
	MSA (H ₂ SO ₄ -MSA-Mix)	7.5	
	H ₂ SO ₄ (H ₂ SO ₄ -MSA-Mix)	44.45	
	Sulfur (recycled from H ₂ S) → can be subtracted from the original sulfur input	131.59	
Emissions/Waste/Recyclables of production process	H ₂ S (70% before treatment)	200.00	
	SO ₂ (Splitting Plant)	0.16	
	CO ₂ (Splitting Plant)	50.08	
	SO ₂ (Claus Process)	0.273	
	NO _x (Claus Process)	0.0001	
	CO (Claus Process)	0.0001	
	Polysulfides (before treatment)	36.16	
	MSA-methyl esters (before treatment)	37.5'0	
	Water (Phase cutter)	283.87	
	Production Process (Thermal)		1611
Energy	Production Process (Electrical)		179
	Claus-Oven (Electrical)		2.06
Materials/Energy: Direct Process		Kg/FU	kWh/FU
Water	Water (Cooling)	5'000.00	
Reaction Materials	Water (pure)	414.14	
	SO ₃	960.00	
	CH ₄	206.25	
	CH ₄ (intermediate; excess substance after reaction, before treatment)	34.37	
Products/Byproducts	H ₂ O ₂	7.50	
	MSA (diluted 70%)	1'414.14	
	MSA (H ₂ SO ₄ -MSA-Mix)	35.00	
	H ₂ SO ₄ (H ₂ SO ₄ -MSA-Mix)	140.00	
Emissions/waste of production process and SO ₃ -production	CO ₂ (burning of methane)	94.31	
	SO ₃ (SO ₃ -Production)	0.021	
	SO ₂ (SO ₃ -Production)	1.22	
	Water	5'331.21	
Energy	Production Process & Waste Treatment (Thermal)		514.80
	Production Process & Waste Treatment (Electrical)		57.20
	SO ₃ – Production (Electrical)		–60.50

Appendix C. Impact categories

This section contains a detailed overview of all impact categories for both production processes. The main contributors to the four largest processes are described and listed in the subsections.

C1. Impact category results conventional process

Impact Category	EIP	Contribution [%]
<i>Total</i>	<i>208.91</i>	<i>100.00%</i>
Fossil Depletion	120.99	57.76%
Climate Change Human Health	44.72	21.35%
Climate Change Ecosystems	28.29	13.51%
Particulate Matter Formation	6.41	3.06%
Human Toxicity	4.83	2.31%
Metal Depletion	1.48	0.70%
Natural Land Transformation	1.48	0.70%
Agricultural Land Occupation	0.93	0.44%
Urban land Occupation	0.16	0.08%
Terrestrial Acidification	0.05	0.02%
Freshwater Eutrophication	0.04	0.02%
Ionising Radiation	0.04	0.02%
Freshwater Ecotoxicity	0.02	0.01%
Ozone Depletion	0.02	0.01%
Terrestrial Ecotoxicity	0.01	0.01%

(continued)

Impact Category	EIP	Contribution [%]
Marine Ecotoxicity	0.00	0.00%
Photochemical Oxidant Formation	0.00	0.00%

Fossil depletion

The main contributors to this impact category are natural gas followed by crude oil and coal. The natural gas is used for the production of methanol and thermal energy (both from Norwegian origin) and to a smaller degree for hydrogen cracking and the production of electrical energy. The hydrogen is later used to form hydrogen sulfide. The crude oil is used in petroleum refineries to produce sulfur which in turn is used for the formation of hydrogen sulfide. Coal is used for the production of electricity.

Impact Source Fossil Depletion	EIP	Contribution [%]	Amount
<i>Total</i>	<i>120.99</i>	<i>57.76%</i>	<i>-</i>
Gas, natural/m3	78.51	37.48%	890.83 m ³
Oil, crude	34.73	16.58%	311.60 kg
Coal, brown	3.91	1.87%	154.92 kg
Coal, hard	3.73	1.78%	84.21 kg
Remaining substances	0.10	0.05%	–

Climate change to human health

Fossil carbon dioxide emissions are the main driving force for this impact category and can mainly be attributed to the generation of electrical and thermal energy. Smaller amounts of the fossil emissions are due to the treatment of byproducts created in the conventional process such as polysulfides and MSA-methyl esters. Other substances with high impact are methane from fossil and biogenic sources and dinitrogen monoxide. The largest source of N₂O emissions is during the production of nitric acid which is used as an oxygen source for the MSA synthesis. Methane emissions from fossil sources are generated during the venting, production and transportation of natural gas as well as its conversion to syngas and methanol. Large amounts of CH₄ emissions are also produced during the mining of coal which is used for the generation of electricity and the cracking of hydrogen which is used in the production of hydrogen sulfide (one of the starting reactants of MSA production). Methane emissions from biogenic sources can mainly be attributed to the production of biogas which is in turn burnt for the generation of electricity.

Impact Source Climate Change to Human Health	EIP	Contribution [%]	Amount [kg]
<i>Total</i>	44.72	21.35%	-
Carbon dioxide, fossil	40.89	19.52%	1475.10
Methane, fossil	2.01	0.96%	2.90
Dinitrogen monoxide	1.61	0.77%	0.195
Methane, biogenic	0.12	0.06%	0.202
Remaining substances	0.08	0.04%	—

Climate change to ecosystems

The substances that carry the main impacts are the same as in the last category.

Impact Source Climate Change to Ecosystems	EIP	Contribution [%]	Amount [kg]
<i>Total</i>	28.29	13.51%	-
Carbon dioxide, fossil	25.87	12.35%	1475.10
Methane, fossil	1.27	0.61%	2.90
Dinitrogen monoxide	1.02	0.49%	0.195
Methane, biogenic	0.08	0.04%	0.202
Remaining substances	0.05	0.02%	—

Particulate matter formation

The main contributing substances here are sulfur dioxide and nitrogen oxides. Nitrogen oxides are emitted to the atmosphere mainly during the formation of nitric acid and during the burning of natural gas for thermal energy. Further NO_x is emitted during the generation of thermal energy and electricity when coal is burned. The sulfur dioxide is formed during sulfur recovery of hydrogen sulfide in the Claus oven and in the splitting plant during treatment of byproducts from the MSA production-process. Other sources of SO₂ emissions are from the production of electricity when burning coal, natural gas and petroleum waste, from the production of sulfur and methanol.

Impact Source Particulate Matter Formation	EIP	Contribution [%]	Amount [kg]
<i>Total</i>	6.41	3.06%	-
Sulfur dioxide	2.24	1.07%	2.18
Nitrogen oxides	2.22	1.06%	1.96
Particulates, < 2.5 µm	1.18	0.56%	0.229
Ammonia	0.39	0.19%	0.240
Particulates, > 2.5 µm, and < 10 µm	0.37	0.17%	0.0712
Remaining substances	0.00	0.00%	—

C2. Impact category results direct process

Impact Category	EIP	Contribution [%]
<i>Total</i>	70.12	100.00%
Fossil Depletion	50.19	71.57%
Climate Change Human Health	9.50	13.55%
Climate Change Ecosystems	6.01	8.57%
Particulate Matter Formation	2.70	3.85%
Natural Land Transformation	0.88	1.25%
Human Toxicity	0.46	0.66%
Metal Depletion	0.23	0.33%
Agricultural Land Occupation	0.06	0.09%
Urban Land Occupation	0.04	0.05%
Terrestrial Acidification	0.03	0.04%
Ionising Radiation	0.01	0.02%
Ozone Depletion	0.01	0.01%
Terrestrial Ecotoxicity	0.00	0.01%
Freshwater Eutrophication	0.00	0.01%
Freshwater Ecotoxicity	0.00	0.00%
Photochemical Oxidant Formation	0.00	0.00%
Marine Ecotoxicity	0.00	0.00%

Fossil depletion

The main contributor to this impact category is natural gas followed by crude oil and coal. Natural gas is used both as a thermal energy source and is the raw material used to extract methane, one of the starting reactants. The crude oil is used in petroleum refineries to produce sulfur which in turn is used to produce sulfur trioxide, one of the main starting reactants of the process. Coal is used for the production of electricity.

Impact Source Fossil Depletion	EIP	Contribution [%]	Amount
<i>Total</i>	50.19	71.57%	-
Gas, natural/m ³	28.32	40.39%	321.38 m ³
Oil, crude	21.09	30.08%	189,266 kg
Coal, brown	0.42	0.59%	14,241 kg
Coal, hard	0.34	0.49%	8,972 kg
Remaining substances	0.01	0.02%	—

Climate change to human health

Fossil carbon dioxide emissions are the major contributor and can mainly be attributed to the generation of electrical and thermal energy. Further 28% of the fossil emissions are produced during the flaring of excess methane in the MSA production process. Other substances with high impact are methane from fossil and biogenic sources and dinitrogen monoxide. Methane emissions can be attributed to the German electrical energy mix used to power the processes and the heat needed from natural gas sources. More specifically the methane emissions come from the mining of hard coal, the venting/transporting of natural gas and the production of biogas. The dinitrogen monoxide emissions are mainly produced during the production of electrical energy by burning lignite and hard coal.

Impact Source Climate Change to Human Health	EIP	Contribution [%]	Amount [kg]
<i>Total</i>	9.50	13.55%	—
Carbon dioxide, fossil	9.09	12.96%	327,745
Methane, fossil	0.37	0.52%	0.527
Dinitrogen monoxide	0.02	0.04%	0.003
Remaining substances	0.02	0.03%	—

Climate change to ecosystems

The substances that carry the main impacts are the same as in the last category.

Impact Source Climate Change to Ecosystems	EIP	Contribution [%]	Amount [kg]
<i>Total</i>	<i>6.01</i>	<i>8.57%</i>	<i>-</i>
Carbon dioxide, fossil	5.75	8.20%	327.745
Methane, fossil	0.23	0.33%	0.527
Dinitrogen monoxide	0.02	0.02%	0.003
Remaining substances	0.02	0.02%	—

Particulate matter formation

The main contributing substances here are sulfur dioxide and nitrogen oxides. Most of the sulfur dioxide emissions are produced during the formation of sulfur trioxide (main starting ingredient for MSA production) and in the petroleum refineries where sulfur itself is won. Smaller amounts of SO₂ are also formed during the production of energy (electrical and thermal). Nitrogen oxides are emitted during the generation of thermal energy and electricity when coal is burned.

Impact Source Particulate Matter Formation	EIP	Contribution [%]	Amount [kg]
<i>Total</i>	<i>2.70</i>	<i>3.85%</i>	<i>-</i>
Sulfur dioxide	1.91	2.72%	1.853
Nitrogen oxides	0.46	0.65%	0.405
Particulates, < 2.5 µm	0.25	0.36%	0.049
Particulates, > 2.5 µm, and < 10 µm	0.08	0.11%	0.015
Remaining substances	0.00	0.01%	

References

- Anastasopoulou, A., Butala, S., Lang, J., Hessel, V., Wang, Q., 2016. Life cycle assessment of the nitrogen fixation process assisted by plasma technology and incorporating renewable energy. *Ind. Eng. Chem. Res.* 55, 8141–8153.
- BASF, S.E., 2011. Lutropur® – the Friendly Acid.
- BASF, S.E., 2012. BASF nimmt Erweiterte Methansulfonsäure/Lutropur® Anlage in Ludwigshafen Erfolgreich in Betrieb. <http://www.care-chemicals.basf.com/press-center/news-detail?id=60a960a0-d2ec-4001-96c7-5549a0733ab1&lang=de>. Accessed February 20, 2018.
- Brand, A., 2003. Production of Alkyl Mercaptans and/or Dialkyl Sulfides, Used in Preparation of Alkanesulfonic Acid, Methionine, Dimethylsulfoxide or Dimethylsulfone, Involves Adding Oxygen During Catalytic Reaction of Alcohol with Hydrogen Sulfide (DE10137773).
- Brand, A., Quasching, V., 2004. Catalyst for the Production of Methyl Mercaptan from Methanol and Hydrogen Sulfide (WO2004096760).
- Caballero, A., Pérez, P.J., 2013. Methane as raw material in synthetic chemistry. The final frontier. *Chem. Soc. Rev.* 42, 8809–8820.

- Eiermann, M., Tragut, C., Ebel, K., 2000. Method of Producing Alkane Sulfonic Acid (WO0031027).
- European Commission, 2007. Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers.
- Fassbender, S., Petersen, P., Lauterbach, A., Renz, G., Borgmeier, F., Kolb, P., 2011. Method for Handling Aqueous Methansulfonic Acid (WO2011054703).
- Gernon, M., 1999. Environmental benefits of methanesulfonic acid. *Comparative properties and advantages*. *Green Chem.* 1, 127–140.
- Gunnar, H., Bechtel, M., Freudenthaler, E., Eiermann, M., 2002. Method for Producing Organic Disulphide (WO20081436).
- Gunsalus, N.J., Koppaka, A., Park, S.H., Bischof, S.M., Hashiguchi, B.G., Periana, R.A., 2017. Homogeneous functionalization of methane. *Chem. Rev.* 117, 8521–8573.
- Guo, X., Fang, G., Li, G., Ma, H., Fan, H., Yu, L., Ma, C., Wu, X., Deng, D., Wei, M., 2014. Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen. *Science* 344, 616–619.
- Haynes, C.A., Gonzalez, R., 2014. Rethinking biological activation of methane and conversion to liquid fuels. *Nat. Chem. Biol.* 10, 331–339.
- Hesse, W., Sterzel, H.-J., Tragut, C., 2000. Method for Producing Organic Disulfides (WO0031029).
- Horn, R., Schlögl, R., 2015. Methane activation by heterogeneous catalysis. *Catal. Lett.* 145, 23–39.
- Jacobs Comprimo Sulfur Solutions. Sulfur Recovery-Claus Process. http://www.jacobs.com/uploadedFiles/wwwjacobscom/20_Learn_About_Us/25_Products/253_Coprismo_Sulfur_Solutions/Technologies/Handout%20Jacobs%20CSS%20-%20Claus%20Process.pdf. Accessed February 21, 2018.
- Kamphus, M., 2014. Emission monitoring in nitric acid plants. *Nitrogen+Syngas* 328, 48–53.
- Manenti, F., Papasidero, D., Bozzano, G., Pierucci, S., Ranzi, E., Buzzi-Ferraris, G., 2013. Total plant integrated optimization of sulfur recovery and steam generation for Claus processes using detailed kinetic schemes. In: *Computer Aided Chemical Engineering*. Elsevier, pp. 811–816.
- McCoy, M., 2016. German firm claims new route to methanesulfonic acid. *Chem. Eng. News* 94, 10.
- McFarland, E., 2012. Unconventional chemistry for unconventional natural gas. *Science* 338, 340–342.
- Nahreneh, S., Praserthdam, S., Perez Beltran, S., Balbuena, P.B., Adhikari, S., Gupta, R.B., 2016. Catalytic upgrading of methane to higher hydrocarbon in a nonoxidative chemical conversion. *Energy Fuel*. 30, 2584–2593.
- Ott, T., Biertümpel, I., 2017. Novel Initiator for Preparing Alkanesulfonic Acids from Alkane and Oleum (EP3071549).
- Ott, T., Biertümpel, I., Bunthoff, K., Richards, A., 2015. Process for Preparing Alkanesulfonic Acids from Sulfur Trioxide and Alkane (WO2015071365).
- Peplow, M., 2017. The great gas gold rush. *Nature* 550, 26–28.
- Piccinno, F., Hischer, R., Seeger, S., Som, C., 2016. From laboratory to industrial scale. A scale-up framework for chemical processes in life cycle assessment studies. *J. Clean. Prod.* 135, 1085–1097.
- Sassi, M., Gupta, A.K.A., 2008. Sulfur recovery from acid gas using the Claus process and high temperature air combustion (HITAC) technology. *Am. J. Environ. Sci.* 4, 502.
- Schwach, P., Pan, X., Bao, X., 2017. Direct conversion of methane to value-added chemicals over heterogeneous catalysts. *Challenges and prospects*. *Chem. Rev.* 117, 8497–8520.
- Woelfert, A., Jachow, H., Driess, H., 2008a. Method and Device for Continuous Production of Hydrogen Sulphide (WO2008087125).
- Woelfert, A., Jachow, H., Driess, H., 2008b. Method and Device for the Continuous Production of Hydrogen Sulfide (WO2008087106).
- Woelfert, A., Jachow, H., Driess, H., 2008c. Reactor and Method for Production of Hydrogen Sulphide (WO2008087086).
- Woelfert, A., Grzonkowski, F., Jachow, H., Renz, G., 2010. Method for Compressing Gases Containing Hydrogen Sulfide (WO2010072756).
- Wu, B., Zhang, X., Xu, Y., Bao, D., Zhang, S., 2015. Assessment of the energy consumption of the biogas upgrading process with pressure swing adsorption using novel adsorbents. *J. Clean. Prod.* 101, 251–261.