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Consequential life cycle assessment of carbon capture and utilization technologies within the chemical industry†

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Carbon capture and utilization is a promising approach to reduce greenhouse gas emissions and fossil resource depletion in the chemical industry. However, since carbon capture and utilization is an energy and material intensive process, it is unclear whether it allows for a net reduction of environmental impacts from a life cycle perspective. Previous life cycle assessment studies on carbon capture and utilization focused on the production of one specific chemical or the comparison of C_1 basic chemicals and applied an attributional approach. This study assesses twelve CO_2-conversion technologies to provide decision support on the potential life-cycle environmental impacts of each technology. Consequential life cycle assessment was chosen as the modeling approach to better understand the system-wide environmental consequences of introducing carbon capture and utilization technologies in the chemical industry. This study has identified that in a near- and a long-term scenario the global warming impact for all CO_2 conversions technologies, besides dimethoxymethane, electrochemically produced formic acid, and Fischer–Tropsch production, is negative. Formic acid produced *via* hydrogenation and polyol production are the conversion technologies with the highest potential for reducing the global warming impact from a life cycle perspective. Holistically polyol production is the conversion technology with the highest potential for reducing environmental impacts. In general, it seems recommendable to introduce carbon capture and utilization within the chemical industry from an environmental perspective.

Broader context

As climate change is one of the major challenges for humankind, climate-mitigating strategies are needed. Carbon capture and utilization is a strategy which is supposedly climate mitigating. Carbon capture comprises the capturing of CO_2 from point sources, such as coal-fired power plants. Utilization of CO_2 comprises the valorization of CO_2 by for instance hydrogenation to methanol. Thus, carbon capture and utilization allows one to decrease direct emissions of point sources and provision of chemicals. However, carbon capture and utilization is an energy demanding strategy. First, capturing CO_2 needs, when using amine scrubbing, thermal energy, which leads to additional greenhouse gas emissions or a decrease in the efficiency of a plant. Second, the valorization of CO_2 is difficult due to its inertness and is an energy intensive process as well. Therefore the CO_2 must be activated by a reducing agent. Energy-intensive water electrolysis produces the widely used reducing agent H_2, which also could hamper the environmental performance of carbon capture and utilization. Besides the possibility of climate mitigation, carbon capture and utilization is a promising strategy for the chemical industry to shift from crude oil based chemistry to CO_2 based chemistry.

Introduction

Carbon capture and utilization (CCU) is a promising approach for reducing emissions of greenhouse gases and depletion of fossil resources, especially in the chemical industry. The potential as a climate mitigation practice for CCU is also mentioned in the recently published report from the Intergovernmental Panel on Climate Change.[1] CCU comprises "*both industrial capture to obtain concentrated CO_2, and separate functional utilization of this CO_2*".[2] The functional utilization contains the direct utilization of CO_2, for example in carbonated beverages, or CO_2 conversion into more complex chemicals, like polymers.[2] However, previous studies have questioned whether CCU provides an environmental benefit, from a life cycle perspective.[2–4]

Existing life cycle assessments (LCA) of CCU investigate the environmental impacts of the production of a chemical, for example, C_1 basic chemicals like carbon monoxide,[5] syngas,[6,7] formic acid,[5,8,9] methane[6,7,10–16] and methanol.[5,6,12–14,17–19] Other LCAs focused on the assessment of more complex molecules produced *via* CCU, like methyl propionate,[20] DME,[11,19,21]

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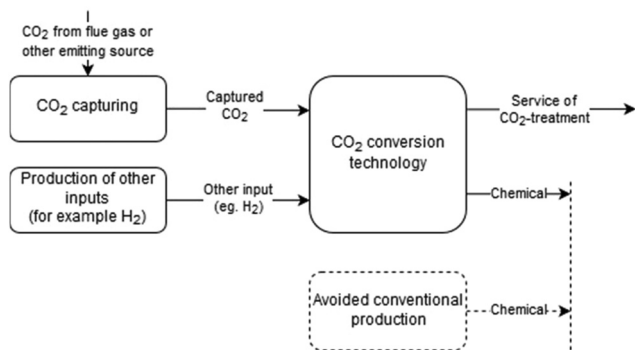† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ee00914k

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Fig. 1 Generalized scheme of the investigated product system.

DMC,[17,22] OME,[23] (jet) fuels,[24,25] and polymers.[4,14,21,26,27] A recurrent conclusion from these studies is that emissions of greenhouse gases are reduced when producing the chemicals *via* CCU while using electricity from renewable resources compared to fossil-based production. However, in one study[22] this is not the case although best-case estimates were taken. Two studies[5,14] compared different CCU technologies and concluded that the production of formic acid[5] and methane[14] achieves the highest environmental impact reductions compared to their conventional production.

Additionally, review studies have been published which comprise the main findings of the environmental assessment of CCU technologies.[28–30] Artz *et al.*[28] conclude that already today production of chemicals with CCU technologies reduces global warming impacts (GWI) compared to conventional production of chemicals from fossil resources. This is the case for CO_2-based polyol production and formic acid production. Cuéllar-Franca and Azapagic[29,30] summarize that the utilization of CO_2 for producing DMC could lower the GWI compared to the conventional production by 4.3 times. Moreover, specific methodological guidance on how to conduct LCA for CCU technologies has been developed.[2,31]

A common trait of previous LCA studies of CCU is that they apply an attributional approach, for example, they use the partitioning method to solve the multi-functionality of the CO_2-supply activity and use an average mix of suppliers for each activity. Attributional models focus on retrospectively attributing impacts to the activities of a product's life cycle based on a normative approach. Instead, consequential models are prospective as they attempt to model as closely as possible the consequences of future decisions. Therefore, consequential LCA appears better suited to the assessment of emerging technologies like CCU, as also mentioned in the previous literature.[4,32] Hence, this study aims to compare CO_2 conversion technologies (*cf.* Fig. 1), which was to the best of our knowledge not done before.

Method

The functional unit chosen for the comparative analysis is the treatment of 1 kg of CO_2. This allows comparing all CO_2-conversion technologies. A functional unit based on the input H_2 would exclude a broad range of conversion technologies from the comparison, such as electrochemical conversion or CO_2-incorporation technologies.[6] The analysis was carried out *via* openLCA 1.7.3[33]
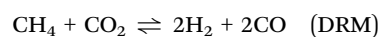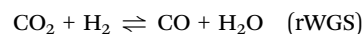
and Brightway2[34] software using background data from the ecoinvent database 3.4 consequential.[35] The scope of the study is limited to German conditions because CCU is already implemented for polyurethane and methane production in Germany. In Germany, several chemical production sites exist and when changing the raw material from fossil-based materials to CO_2 decision support is needed. Hence, if available, we have used background data from Germany. Otherwise, we use data on a European or global background. The details of the life cycle inventory (LCI) are provided in the ESI.† The study focuses on the GWI of different CCU technologies. However, results are as well provided for the midpoint impact categories (IC) freshwater and terrestrial acidification, freshwater ecotoxicity, freshwater eutrophication, ionising radiation, marine eutrophication, terrestrial eutrophication, carcinogenic effects, human health (non-carcinogenic effects), human health (ozone layer depletion), photochemical ozone creation, respiratory effects, land use and mineral, fossils and renewables. Results are calculated using the International Life Cycle Data system 1.0.8 (2016) life cycle impact assessment method.[36]

Fig. 1 shows the structure of the product system under analysis. CO_2 from flue gas or any other emitting source is captured and utilized together with other compounds (like H_2 or natural gas) for the CO_2 conversion. The determining product and main function of the CO_2 conversion technologies are the service of treating CO_2. The conversion technologies produce then chemicals (like methanol) as dependent co-products. Applying the substitution method, the marginal production of the same amount of an identical chemical is avoided. This is in-line with ISO 14040/44, which standardizes LCA practices and recommends to apply system expansion when subdivision of processes is not possible.[37]
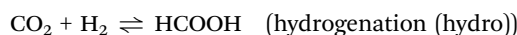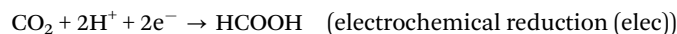
CO_2-Conversion technologies under study

The CO_2-conversion technologies were chosen according to their technology readiness level (TRL), based on their potential to substitute the crude oil-based production of a specific chemical with its CO_2-based production alternative, and the quality of data. Technologies with a TRL lower than three were excluded. Production of urea is excluded since the commercial production technology is already based on CO_2 as a feedstock. Data on technologies available solely on the lab-scale were also excluded. Table S2 (*cf.* file CCU-SI.docx, ESI†) contains a comprehensive summary of CO_2-conversion technologies containing the TRL, reaction parameters and catalysts. The chosen technologies are explained briefly in the following.

Carbon monoxide (CO). Carbon monoxide is mostly utilized with H_2 as syngas for the production of chemical intermediates (*e.g.*, methanol).[38] Conventionally carbon monoxide is produced by gasification of coal, steam reforming or partial oxidation of hydrocarbons.[38] The investigated CO_2-based production technologies of carbon monoxide in this article are the reverse water gas shift (rWGS) reaction[39] and dry reforming of methane (DRM).[40]

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (rWGS)$$

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO \quad (DRM)$$

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**Formic acid (FA).** Due to its acidity, reducing properties and aldehydic nature, formic acid is applied in a wide range of application fields. European formic acid is mostly used in the feed industry and as a silage aid.[41] The potassium salt of formic acid is used on a large scale for the de-icing of aircraft. Today mainly two production technologies are applied for producing formic acid. Methyl formate hydrolysis on the one and preparation of free formic acid from formates on the other hand.[41] For the CO_2-based reaction to formic acid, two technologies are considered. Firstly, formic acid production *via* electrochemical reduction of CO_2[8,9,42] and, secondly, the hydrogenation of CO_2 is considered.[43]

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \quad \text{(electrochemical reduction (elec))}$$

$$CO_2 + H_2 \rightleftharpoons HCOOH \quad \text{(hydrogenation (hydro))}$$
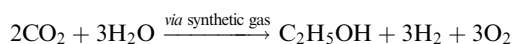
Methanol (MeOH). Methanol is commercially produced from synthesis gas containing CO and H_2.[44,45] As an intermediate product methanol is used in a variety of chemical syntheses, mostly for the production of formaldehyde, methyl *tert*-butyl ether and acetic acid.[44] CO_2-Based production technologies include the hydrogenation of CO_2, which is investigated further.[19,46]

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad \text{(hydrogenation)}$$
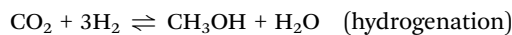
Methane (CH_4). Natural gas mainly contains methane with a molar fraction of up to 0.99.[47] Conventionally, natural gas is extracted either from reservoirs containing oil and gas or from reservoirs containing only gas.[48] Natural gas can be used either as a fuel or as a feedstock in the chemical industry. The application of natural gas as a fuel comprises utilization as a source of heat within residential, commercial and industrial applications. The largest chemical treatment is the production of synthesis gas containing carbon monoxide and H_2.[48] The investigated technology is based on the so-called power-to-gas or power-to-methane technology and produces a methane-rich gas which is also called synthetic or substitute natural gas.[49]

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \text{(Sabatier-reaction)}$$
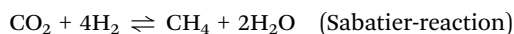
Ethanol (EtOH). Fermentation accounts for 90% of the total ethanol production share whereas 10% of the total ethanol production is produced synthetically from ethylene or as a by-product of specific industrial processes.[50] Ethanol from fermentation is traditionally used for beverages and specialty chemicals whereas ethanol from chemical synthesis is used for industrial purposes.[51] CO_2-Based ethanol is produced from CO_2 and H_2O *via* synthesis gas using co-electrolysis[52] and by fermentation of CO_2 containing syngas in particular in steel mills.

$$2CO_2 + 3H_2O \xrightarrow{\textit{via} \text{ synthetic gas}} C_2H_5OH + 3H_2 + 3O_2$$

Dimethyl ether (DME). Commercially DME is produced by the dehydration of methanol in the presence of acidic catalysts.[53,54] Around 70% of DME is used in the aerosol industry as a propellant and the remaining 30% is used for the production of dimethyl

sulfate.[53] The chosen CO_2-based technology is the direct production of DME *via* synthesis gas and methanol as intermediates.[11]

$$CO_2 + CH_4 + 2H_2 \rightleftharpoons CH_3OCH_3 + H_2O$$
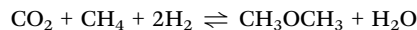
Dimethyl carbonate (DMC). Currently, DMC is mostly produced by the Eni process through oxidative carbonylation of methanol, which replaced the traditional manufacturing production of DMC using toxic phosgene.[22] The application fields of DMC are the synthesis of pharmaceuticals, agricultural chemicals, dyestuffs and usage as a specialty solvent.[55] There are a variety of CO_2-based production technologies for DMC.[22,28] In this article we consider the direct synthesis from CO_2 and methanol to form DMC.[56]

$$CO_2 + 2CH_3OH \rightleftharpoons DMC + H_2O$$
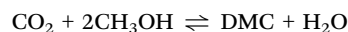
Dimethoxymethane (DMM). Conventionally DMM is produced *via* acid-catalyzed condensation of formaldehyde and methanol.[57] The main applications of DMM are as a precursor to several polymers, as a solvent, and as an ion exchange resin.[28] CO_2-based DMM production starts from H_2 and CO_2 and methanol as a solvent.[23]

$$3CO_2 + 8H_2 \xrightarrow[\text{reduction}]{-2H_2O} CO_2 + 2CH_3OH + 2H_2 \xrightarrow[\text{reduction}]{-2H_2O} DMM$$
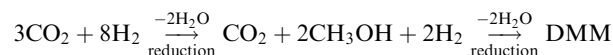
Fischer–Tropsch (FT)-products. The FT-process enables the direct production of liquid hydrocarbons using CO_2 and H_2.[28] Depending on the reaction temperature of the FT-process the product composition changes. With high-temperature FT-processes, fuels can be produced.[58] In this article, we consider an FT-process which produces jet fuel (kerosene) with naphtha as a by-product.[24]

$$nCO_2 + (3n + 1)H_2 \rightarrow C_nH_{2n+2} + 2nH_2O$$

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{n+2} + nH_2O$$
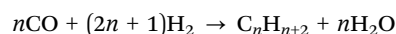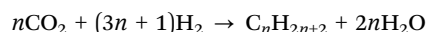
Polyols. Polyether polyols conventionally are produced by a synthesis of propylene oxide, glycerol, and monopropylene glycol.[59] Polyols are used for the production of polyurethane foams and potentially as transparent films and elastomers.[28,60] CO_2-based polyether polyol is formed similarly to the conventional synthesis; however, propylene oxide is partly substituted by CO_2.[27]

Marginal suppliers

An LCI model built according to the consequential approach[61] should reflect the consequences of a specific decision.[62] Only suppliers that are affected by the decision should be included in the system. These are called marginal suppliers, technically defined as suppliers that can respond to a marginal increase in demand for the product.[63] In order to identify the marginal suppliers for CO_2 and H_2, we followed the five-step-procedure explained in Weidema *et al.*[63]

Carbon dioxide. CO_2 can be either captured from point sources or the atmosphere.[2] CO_2-point sources are stationary industrial processes such as fermentation, H_2 production or combustion of fossil fuels.[64] Additionally CO_2 could be obtained

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from the atmosphere *via* so-called direct air capture.[65] CO_2 is currently used in applications such as a feedstock, chilling agent, and solvent in industrial applications like food and beverage manufacturing, pharmaceutical manufacturing, polymer and chemical synthesis, pH control, welding, solvent extraction, and heat pumps.

For the supply of CO_2, a distinction must be made between merchant and captive markets. In the merchant market suppliers sell their CO_2 on the free market. In industrialized countries, CO_2 for the merchant market is mostly captured as a by-product from the production of ammonia, H_2, ethanol, ethylene oxide, and titanium dioxide in high purity. CO_2 is captured from the flue gases of fossil fuel combustion only in pilot plant facilities.[66] On the captive market, the supplier and buyer of a commodity are usually owned by the same entity or distribute the commodity in bulk to a niche market.[66]

According to Supekar and Skerlos (2014),[66] the current capacity of merchant CO_2 exceeds the demand and many high-purity sources are currently operating without CO_2 capture and could supply additional demand for CO_2 in the future. In the near-term, a marginal increase in the demand of CO_2 will be satisfied by high-purity sources currently operating without capture of CO_2. In the long-term, a marginal increase in CO_2 demand will be satisfied *via* the installation of additional plants

for CO_2 capture. Thus, this study considers two scenarios for CO_2 supply: near-term and long-term. According to Naims (2016), the demand in the near-term could be up to 250 Mt and in the long-term up to 2300 Mt of CO_2.[67] Aligning the respective costs for captured CO_2 depending on the point sources and the potential capturable CO_2 emissions per year leads to the CO_2 cost curve in Fig. 2 reproduced from Naims (2016). Matching with the amount of the near- and long-term scenarios leads to the marginal suppliers for each scenario. For the near-term scenario, the marginal supply of CO_2 is from fermentation,[66] bioenergy,[68] production of H_2[66] and production of ammonia.[66] For the long-term scenario, the marginal supply of CO_2 is from the production of ammonia,[66] iron and steel,[69] ethylene[70] and cement.[71] The relative share of each supplier in the total supply (marginal mix) is calculated based on the potentially suppliable amount of CO_2. For the marginal supplier in the long-term scenario, we assume that emitting sources considered in the near-term will not be able to supply any more CO_2 since their capacity will be already fully utilized. The composition of the marginal supply mix for captured-CO_2 is provided in Table S3 (*cf.* file CCU-SI.docx, ESI†).

Hydrogen. H_2 is one of the essential raw materials in the chemical industry and is handled in reactions either by addition, also called hydrogenation, or as a reducing agent.[72] H_2 is utilized for the production of ammonia, methanol, hydrocarbons,
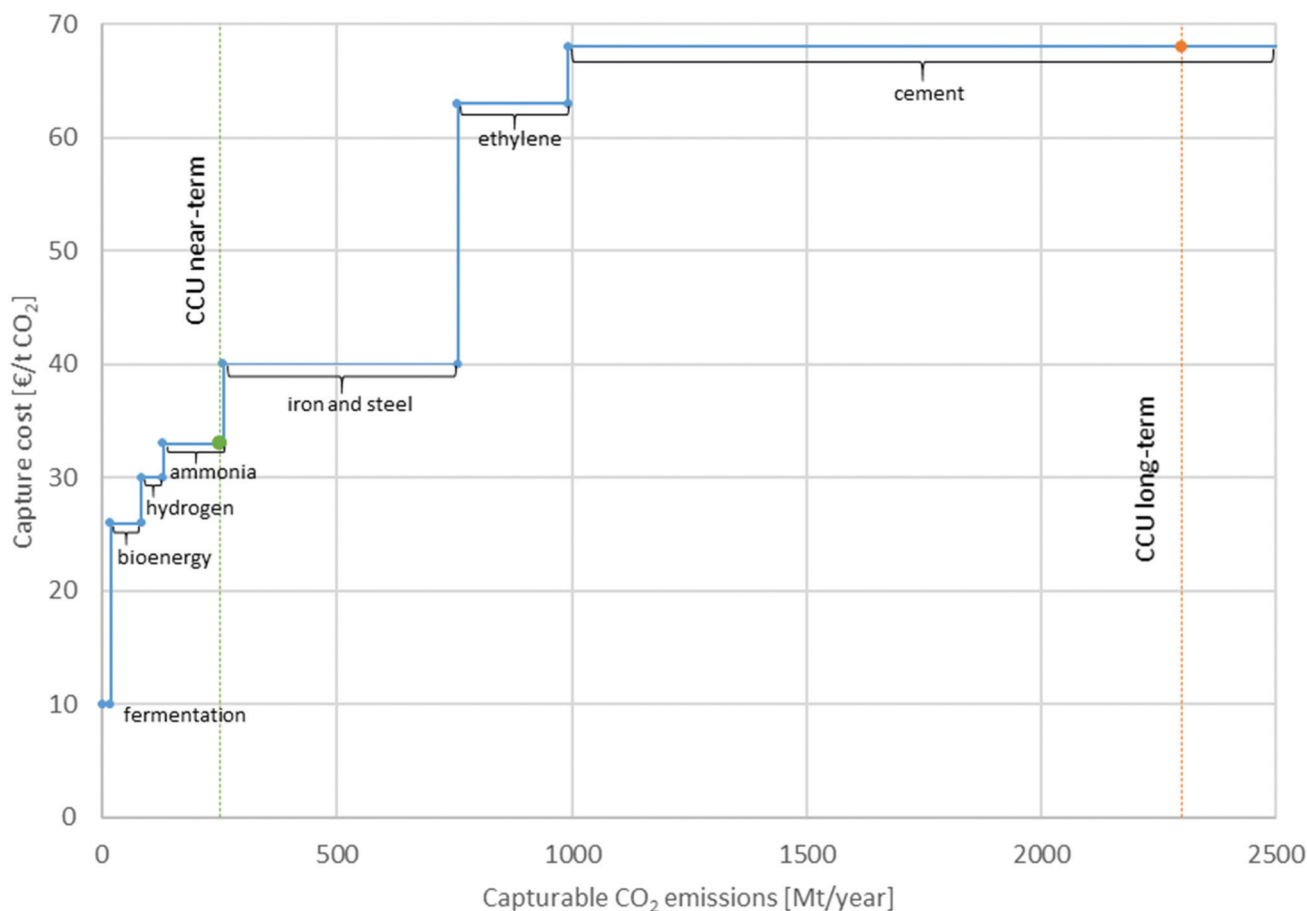

Fig. 2 CO_2 supply and demand scenarios without fossil-fired power generation, adopted from Naims (2016).[67]

and oxo synthesis products. Besides these applications, H_2 is applied in refineries for hydrotreating and hydrocracking.[72] The latter is the enabling technology for converting heavy and sour crude oil as well as for maximizing the yield of the middle distillate from vacuum gas oil produced in a refinery.

The market for H_2 is separated into the captive and merchant H_2 supply.[72] Captive H_2 is produced on-site and directly consumed for ammonia or methanol production of refineries. Merchant H_2 is sold on the free market and accounts for 10% of the total H_2 production.[72] Globally the H_2 supply is composed of natural gas steam reforming (50%), oil reforming (30%), coal gasification (18%), chloralkali electrolysis (3.9%) and other sources (0.1%).[73]

For H_2 production, near- and a long-term scenarios are considered. For the near-term scenario, we assumed the default marginal supplier of H_2 from the ecoinvent database 3.4 consequential. In this dataset, H_2 is produced *via* cracking of fossil fuels. H_2 produced *via* chloralkali electrolysis is constrained and cannot fulfill an increased demand for H_2. Consequently, H_2 production *via* chloralkali-electrolysis is not considered in the chosen dataset.[35] For the long-term scenario, we assumed that the production of H_2 changes to a production technology which is operated with renewable materials. Hence, we identified water electrolysis *via* a proton exchange membrane (PEM) as the H_2-supplier for the long-term scenario. For the production of 1 kg H_2 54.6 kW h electricity and 9.1 kg water are needed.[74] As a by-product, 8 kg oxygen (O_2) is produced and substitutes the conventional production of O_2 *via* cryogenic air separation.[35,74]

Background system. Electricity and heat are the main auxiliary materials needed in the CO_2 conversion process. To model the related production activities, we used data from the ecoinvent database 3.4 consequential. The marginal German market mix was used to model the electricity supply; this mix is composed primarily of electricity from wind (75%) and natural gas (19%). As a heat supplier, we chose the market of heat supply from steam within the chemical industry. Data on the energy demand for each technology under analysis were retrieved from the literature. The authors of these previous studies had either calculated such energy demand with simulation tools (Aspen Plus, CHEMCA, UniSim), or approximated it by the Gibbs free energy, or taken the value from the literature. Finally, we used background market activities to model the production of additional auxiliary materials needed for the CO_2-based chemical production (natural gas, steam, water, refrigerant, and methanol) and to model the avoided production of conventional chemicals. Detailed information on all background datasets used in the model can be retrieved from the inventory data (*cf.* file CCU-LCI.xlsx in the ESI†).

Assumptions for sensitivity and uncertainty analysis

Sensitivity analysis. The uncertainty associated with the modeling choices was investigated by changing assumptions that have or are expected to have a strong influence on the results. As given in the LCA literature, supply of electricity and heat is a significant contributor to the total impact of CCU.[5,7,10,13,14,16,22–25,75] For the electricity supply, we assumed the marginal German market mix as the default provider and

tested how the results changed when assuming that the provision of electricity is solely from lignite (as a worst case) and solely from wind (as a best case). For the heat supply, we assumed the provision of heat within the chemical industry as the default provider. Then we tested how the results changed according to changes of the heat supply. We varied between heat suppliers from central or small-scale combined heat and power plants with and without natural gas as a fuel and heat supply from district or industrial sources with and without natural gas as a fuel.

Uncertainty analysis. The uncertainty associated with the results which depend on the uncertainty of the background model parameters was quantified by applying error propagation *via* Monte Carlo simulation. Values of parameter uncertainty taken directly from ecoinvent database 3.4 consequential were assumed for background exchanges, whereas no uncertainty values were used for foreground exchanges as the focus was on understanding the uncertainties related to the use of background data, while the significant uncertainties in the foreground system were addressed *via* sensitivity analysis (*cf.* the previous section). Characteristic results were calculated for each technology with 1000 iterations with dependent sampling.[76] Statistical pairwise analysis of the differences between technologies was conducted *via* the pairwise Wilcoxon Rank Sum test as in Henriksson *et al.*.[77] The Monte Carlo simulation was performed using the Brightway2 open source LCA software.[34] The statistical analysis was conducted in the R Statistical Environment.[78] All code used in this study is either available on request to the author or openly available online.[79]

Results and discussion

Global warming impact of CO_2-conversion technologies

Fig. 3 shows the GWI for the technologies under analysis in the near- and the long-term scenarios. All technologies result in carbon savings except for the electrochemically produced formic acid, production of FT products, and the DMM production in the long-term. Formic acid produced *via* hydrogenation and polyol production show the lowest GWI. However, the difference between formic acid (hydrogenation) and the polyol technology is not significant when considering the uncertainty (*cf.* the Uncertainty analysis section). Nevertheless, these two production technologies are substantially better than the remainder.

The results can be explained by the ratio of CO_2 to H_2 needed for producing formic acid. While 1 mol CO_2 and H_2 is needed to form formic acid, the ratio of CO_2 to H_2 for methane production is less efficient, as 4 mol of energy-intensive produced H_2 and 1 mol of CO_2 are needed to form 1 mol of methane. Additionally, the formation of formic acid is the only technology for producing basic chemicals where no by-products are produced. In all other production technologies, water is obtained as a by-product, *i.e.*, when producing 1 mol of methane 2 mol of water are formed, which is an indication of a less efficient conversion than the conversion to formic acid. In the case of formic acid conversion, the avoided marginal production has a higher GWI (-4.52 *vs.* -4.49 kg CO_2-eq per kg captured CO_2) compared to

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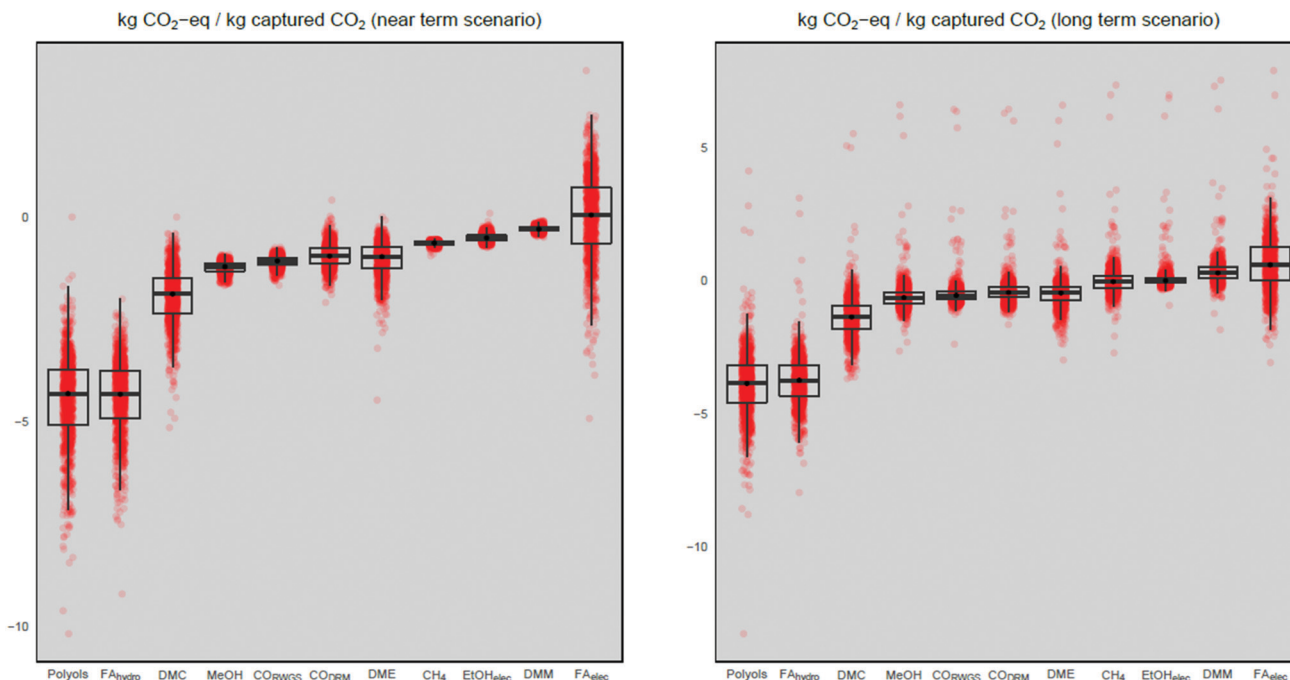*Energy Environ. Sci.*, 2019, **12**, 2253–2263 | **2257**

Fig. 3 Global warming impact of CO_2-conversion technologies (results for FT are excluded here for readability reasons and can be accessed in the ESI†).

other avoided marginal production. This is in accordance with the results of previous studies.[5] However, the electrochemical production of formic acid leads to a positive GWI due to the high thermal energy demand (35.79 kg CO_2-eq per kg captured CO_2) needed for the distillation of the low-concentration formic acid solution (4.5 wt%) obtained from the electrochemical reactor. For the polyol production, the reason for the low GWI compared to the other CO_2 based technologies is that CO_2 is incorporated in the polymer. Hence, CO_2 incorporation avoids the production of a high impact chemical, which is the case for the polyol production in the marginal production technology. These findings are in accordance with results from a previous study.[28]

All results for the long-term scenario lead to higher impacts than those for the near-term scenario, but the ranking of technologies did not change. This increase in impacts is due to the different marginal market mix used in the long-term scenario for the supply of CO_2. In the long-term, CO_2-sources where CO_2 is more diluted are included in the suppliers' mix. Hence, the CO_2-capturing process in the long-term has higher energy-intensity and higher impacts compared to the high-purity CO_2 sources of the near-term mix. The GWI for the marginal market mix of CO_2 for the near-term is −0.80 kg CO_2-eq per kg captured CO_2 (mean = −0.80; standard deviation = 0.01; median = −0.79) and for the long-term −0.34 kg CO_2-eq per kg captured CO_2 (mean = −0.35; standard deviation = 0.06; median = −0.34). This contradicts the idea of postponing CCU since CO_2 capture pursued today would allow emitting fewer greenhouse gases compared to future capture. In the long-term scenario, H_2 is supplied by PEM water electrolysis. The GWI for the marginal market mix is 1.70 kg CO_2-eq per kg H_2 (mean = 1.70; standard deviation = 0.00; median = 1.70) and for the PEM in the long term

is 1.90 kg CO_2-eq per kg H_2 (mean = 1.97; standard deviation = 1.06; median = 1.93). Hence, the impacts of CCU technologies using H_2 are slightly higher due to the higher impacts of H_2 production in the long-term. Still for all but the production of DMM, electrochemically produced formic acid and FT-products in the long-term CCU is an option leading to negative GWI.

Contribution analysis

The activity with the most significant contribution to the GWI is the avoided production of chemicals (see Fig. 4). This is the case for nine technologies in the near and ten technologies in the long-term scenario and especially for technologies producing formic acid, polyols, and DMC. The supply of CO_2 is the second largest contributor to the total GWI of each technology. Electricity and heat generation are the third largest contributor to the total GWI. The provision of H_2, which is mentioned in the literature as one of the major contributors for CCU-systems, has a rather low impact within our study. This is explained by the fact that in the near-term the H_2 is supplied by the market mix of H_2 and in the long-term H_2 supply *via* PEM electrolysis is assumed. The electrolysis – although based on energy-intensive water splitting – utilizes electricity supplied from the marginal electricity mix, which is primarily composed of electricity from wind (75%) and natural gas (19%). H_2-Supply is, thus, a rather low greenhouse gas emitting process.

Further environmental impacts of CO_2-conversion systems

Analyzing the correlation of the GWI with the other impacts shows the categories where further analysis is needed. The values of the correlation analysis and the rankings of each technology in each IC are provided in the ESI† (*cf.* file CCU-LCIA.xlsx). A high
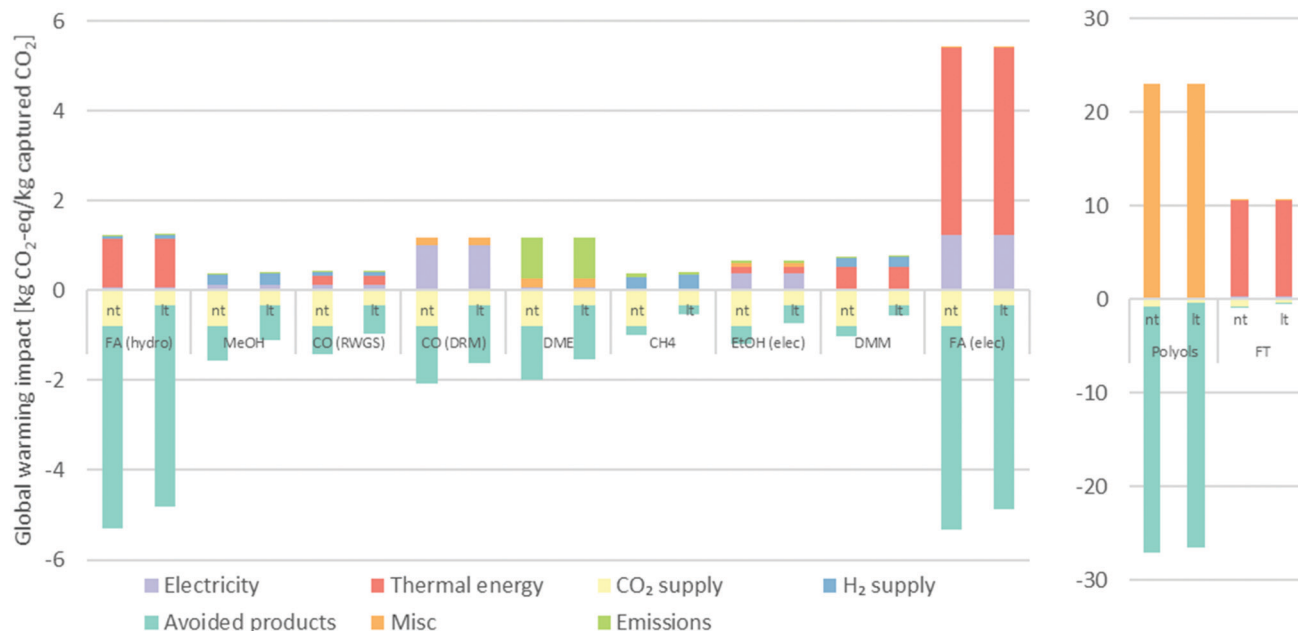
Fig. 4 Contribution analysis for the global warming impact of CO_2-conversion technologies (divided into two graphs due to different scales).

correlation ($R^2 > 0.93$) was observed for GWI and freshwater, terrestrial acidification, freshwater, marine, and terrestrial eutrophication, as well as photochemical ozone creation. These categories are not further discussed as they show the same ranking of the technologies as the GWI. The observed correlation between GWI and other IC was lower ($R^2 < 0.93$) and therefore the ranking of the technologies changed for those IC compared to the GWI. Thus these IC need to be discussed further. Compared to the climate change impact category, a substantially different ranking of alternatives and of process contributions was observed for the case of freshwater ecotoxicity, ecosystem quality, human health (ionizing radiation) and resources (minerals, fossils and renewables).

The production of electricity is the largest contributor to the freshwater ecotoxicity impact and this contribution can be traced back to the construction of windmills and from there to the market for scrap copper. Copper is hazardous and therefore a substance which leads to ecotoxicity impacts. Moreover, impacts from the avoided products contribute to the ecotoxicity impact. For the impact of ionizing radiation on ecosystem quality, the contribution from CO_2 is lower compared to GWI and the contribution from the avoided product is higher compared to GWI. The impacts of ionizing radiation on human health are influenced by the avoided production. This is the case for all technologies except the conversion to produce methane. In the case of the conversion technology for producing methane, the main contributing activity is the CO_2 supply. Impacts on resources (mineral, fossils, and renewables) are directly dependent on the impact of the avoided product. Additionally, for the conversion technology to produce polyols the provision of the needed input materials like propylene oxide is the other main contributor (47% of the overall impact). In summary, polyol production remains the most promising option for

CCU as the average ranking is the highest rank compared to the other CO_2-conversion technologies.

Difference between the near- and long-term scenarios

The ranking for the technologies changed for 13 IC from the near- to the long-term scenario. However, for the GWI and marine eutrophication, the ranking was still the same as for the near term. As only the processes for CO_2- and H_2-supply were changed, differences in the ranking between scenarios are traced back to those processes. Substantial changes in the ranking of the technologies compared to the near term are observed for the IC ecotoxicity, due to the high influence of the electricity mix for producing H_2 in the long term. Another IC for which different rankings are observed in each scenario is human health (ionizing radiation). This is explained by the fact that CO_2-supply in the long term has a lower impact on human health (ionizing radiation) and thus the impact on ionizing radiation is reduced drastically for all technologies using H_2. That is why for instance the treatment of CO_2 to produce CH_4 changed from the 6th best technology to the most favored technology considering human health (ionizing radiation).

Sensitivity analysis

We changed the electricity and heat sources in the near-term to understand how this modeling choice affects the results (*cf.* Table 1). The results show that they are more sensitive to the choice of electricity supplier than to the choice of heat supplier. For ten out of twelve technologies the GWI is at least 10% higher or lower compared to the default scenario (near-term) when changing the electricity supplier. In the case of changing the heat supply, six out of twelve technologies indicate at least 10% higher or lower GWI compared to the default scenario. However, there are also technologies which are more sensitive to changes in heat supplier than in electricity supplier. This is

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Table 1 Sensitivity analysis for heat and electricity supply; absolute values for the deviation from the default in kg CO_2-eq

	CH_4	CO_{DRM}	CO_{dwgs}	DMC	DME	DMM	$EtOH_{dec}$	FA_{dec}	FA_{hycfro}	FT	MeOH	Polyol
Heat supply												
Central or small-scale, natural gas	−0.01	0.00	−0.08	−0.32	−0.01	−0.19	−0.06	−1.47	−0.39	−3.61	−0.01	−0.01
Central or small-scale	−0.03	0.01	−0.21	−0.84	−0.03	−0.49	−0.17	−3.87	−1.02	−9.53	−0.03	−0.03
District or industrial, natural gas	0.01	0.00	0.08	0.33	0.01	0.19	0.06	1.50	0.39	3.69	0.01	0.01
District or industrial	0.01	0.00	0.08	0.32	0.01	0.19	0.06	1.49	0.39	3.66	0.01	0.01
Electricity supply												
Lignite	0.26	8.40	1.20	0.14	0.64	0.28	3.32	10.13	0.72	2.20	1.14	0.21
Wind	−0.03	−0.85	−0.12	−0.01	−0.06	−0.03	−0.34	−1.03	−0.07	−0.22	−0.12	−0.02

the case for the conversion technologies to CO *via* rWGS, DMM, EtOH, formic acid *via* hydrogenation and FT-products. The GWI for conversion technologies to produce CH_4, CO *via* DRM, DME, formic acid *via* electrochemical reduction and MeOH is sensitive to changing the electricity supplier. The GWI for CO_2-conversion to DMC is sensitive to changing the heat supplier.

Interestingly, for the conversion technology producing polyols, the GWI is insensitive to changes in the electricity or heat supplier. This is because the main contributing processes to the overall GWI for polyol production are the provision of the feedstocks besides CO_2 (46%) and the avoided burden for substituting the marginal production of the polyols (52%). Consequently, the contribution to the overall GWI is rather low for the supply of heat and electricity when producing polyols.

Uncertainty analysis

The testing for differences between alternatives shows that due to the uncertainties in the background data some comparisons were not statistically significant. In the near-term scenario, we cannot conclude that the treatment of CO_2 to produce polyols is significantly different from the treatment of CO_2 to produce formic acid by hydrogenation ($p = 1$). Another non-significant difference is between CO_2 conversion into dimethyl ether and carbon monoxide *via* DRM ($p = 0.410$). Similarly, in the long-term scenario, we cannot find a significant difference between the treatment of CO_2 to produce polyols and the treatment of CO_2 to produce formic acid by hydrogenation ($p = 0.749$) and between CO_2 conversion into dimethyl ether and carbon monoxide ($p = 1$). Additionally in the long-term scenario we cannot conclude that the impact of the treatment of CO_2 to produce ethanol is significantly different from the impact of the treatment of CO_2 to produce methane ($p > 0.0001$) and there is no observed strong difference between CO_2 conversion into dimethyl ether and carbon monoxide *via* rWGS ($p = 0.0000116$). It can, therefore, be concluded with strong confidence that technologies for producing formic acid and polyols have a significantly lower global warming impact than the other technologies. Full results of the statistical testing are provided in the ESI† (*cf.* file CCU-UA.xlsx).

Study scope, assumptions, and validity

The validity of these results should be discussed in light of the scope of the study and its main assumptions. The study focused on CCU technologies with a TRL equal to or higher than three, replacing a fossil-based production technology, and with data available beyond the lab scale. However, new data on lower tier

technologies might be available in the near future, as conversion technologies currently experience substantial development. This new evidence could be used to improve the current analysis possibly leading to different conclusions. Data on technologies with a lower TRL than three were deemed too uncertain to be used in this comparative context, and appropriate techniques, for example technology upscaling, should be applied when using such data, but this was beyond the scope of the current study.[80] New or systemic process designs for CCU technologies, for example by including heat integration or downstream processing, could, for example, change our results drastically (*e.g.*, building a plant which only uses solar energy in this specific case).

Additionally, the study did not focus on the impacts generated from the production of catalysts and infrastructure, since the contribution of such activities is expected to be rather small compared to the impacts coming from primary inputs like electricity, heat, and CO_2 supply.[81]

Within the study, the best available knowledge was applied to identify the marginal suppliers. As there is yet no established market for CO_2, the identification of marginal supplier for CO_2, especially in the long-term, is dependent on several assumptions. However, a change in the CO_2 marginal supplier would change the results of all technologies and therefore should not change the overall conclusions. Additionally, the choice to assess H_2 from PEM as a marginal supplier was motivated by pragmatic reasons, given that market studies forecasting future H_2 suppliers are scarce. Despite these assumptions, this study offers insights into the environmental assessment of CCU technologies which are in line with results of previous studies[5,28] and extend current CCU technology knowledge.

Conclusions

This study determined the life-cycle impacts of CO_2 conversion technologies to support the choice between different CO_2 conversion technologies from an environmental perspective and with a particular focus on climate-related impacts. The main highlight is that a negative GWI was observed for all CO_2 conversion technologies besides DMM, electrochemically produced formic acid, and FT production, in both a near- and a long-term scenario. The research has also shown that formic acid produced *via* hydrogenation and polyol production are the CCU conversion technologies with the highest reduction potential in terms of GWI. The second significant finding was that holistically

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polyol production is the CO_2 conversion technology with the highest potential for reducing the climate impact. Based on these findings it seems recommendable to introduce CCU within the chemical industry from an environmental perspective. This research is the first comprehensive investigation of comparing CO_2 conversion technologies within a broad scope and lays the ground for future work in the field of environmental assessment of CCU.

Additionally, the study contributes to our understanding of the environmental consequences of introducing CO_2 conversion technologies by assessing the environmental impacts with the consequential LCA approach. The question raised by this study is a rather general question on the introduction of CCU in the chemical industry. Further research should, therefore, determine environmental impacts by using a consequential LCA approach on a site-specific basis (*e.g.*, environmental assessment of an existing CCU pilot plant).

Abbreviations

CCU	Carbon capture and utilization
DMC	Dimethyl carbonate
DME	Dimethyl ether
DMM	Dimethoxymethane
DRM	Dry reforming of methane
elec	Electrochemical reduction
EtOH	Ethanol
FA	Formic acid
FT	Fischer–Tropsch
GWI	Global warming impact
hydro	Hydrogenation
IC	Impact category
LCA	Life cycle assessment
LCI	Life cycle inventory
MeOH	Methanol
PEM	Proton exchange membrane
rWGS	Reverse water gas shift
ESI	Electronic supplementary information
TRL	Technology readiness level

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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