White Rose Research Online

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk
Universities of Leeds, Sheffield and York

Deposited via The University of Sheffield.

White Rose Research Online URL for this paper:
https://eprints.whiterose.ac.uk/id/eprint/170499/

Version: Published Version

Article:
Garcia-Garcia, G., Fernandez, M.C., Armstrong, K. et al. (2021) Analytical review of life-cycle environmental impacts of carbon capture and utilization technologies. ChemSusChem, 14 (4). pp. 995-1015. ISSN: 1864-5631

https://doi.org/10.1002/cssc.202002126

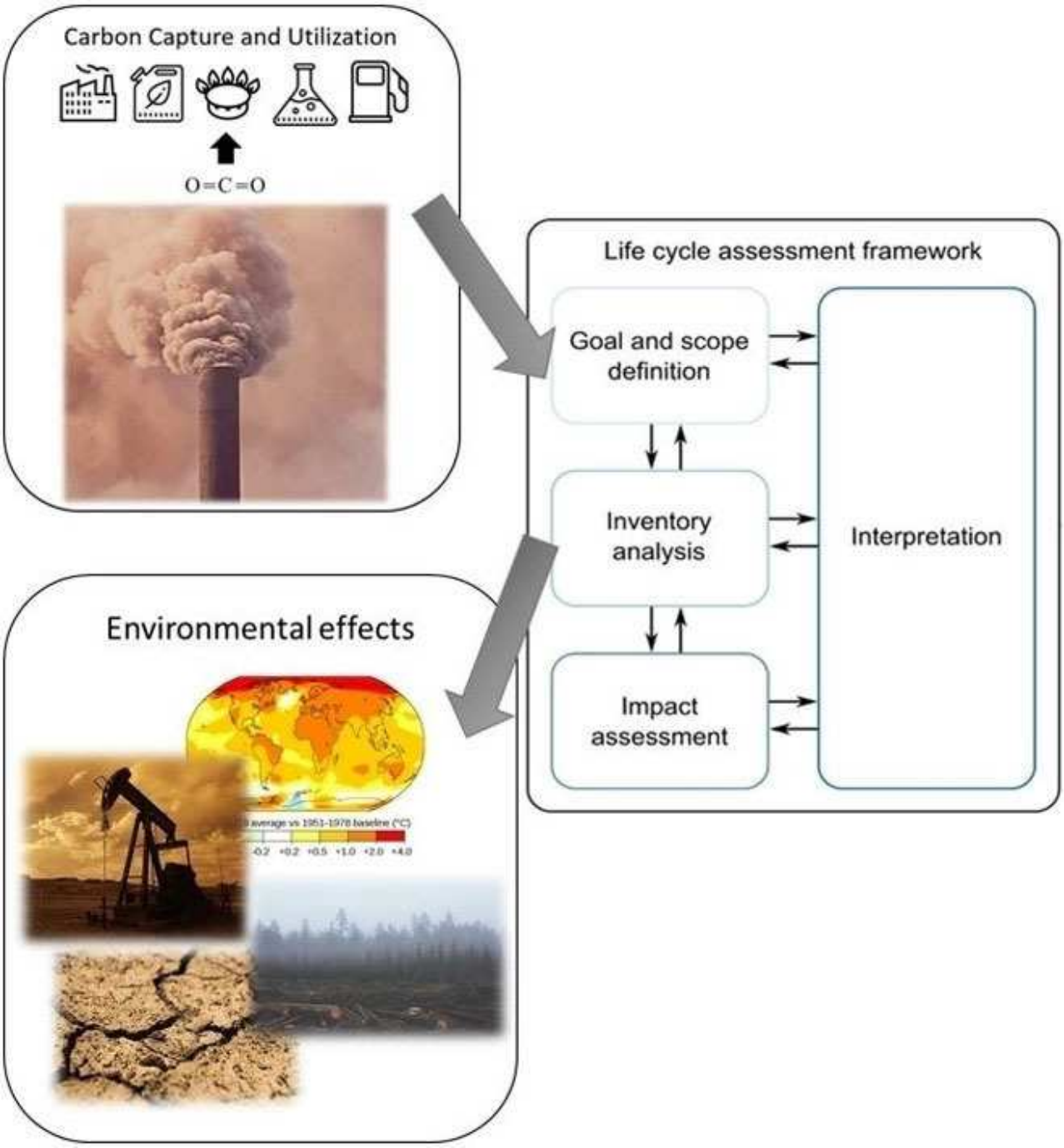
Reuse
This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: https://creativecommons.org/licenses/

Takedown
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

doi.org/10.1002/cssc.202002126
Check for updates
Chemistry Europe
European Chemical Societies Publishing

Analytical Review of Life-Cycle Environmental Impacts of Carbon Capture and Utilization Technologies

Guillermo Garcia-Garcia,[a] Marta Cruz Fernandez,[b] Katy Armstrong,[a] Steven Woolass,[b] and Peter Styring*[a]



© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Carbon capture and utilization (CCU) has been proposed as a sustainable alternative to produce valuable chemicals by reducing the global warming impact and depletion of fossil resources. To guarantee that CCU processes have environmental advantages over conventional production processes, thorough and systematic environmental impact analyses must be performed. Life-Cycle Assessment (LCA) is a robust methodology that can be used to fulfil this aim. In this context, this article aims to review the life-cycle environmental impacts of several CCU processes, focusing on the production of methanol, methane, dimethyl ether, dimethyl carbonate, propane and propene. A systematic literature review is used to collect relevant published evidence of the environmental impacts and potential benefits. An analysis of such information shows that CCU generally provides a reduction of environmental impacts, notably global warming/climate change, compared to conventional manufacturing processes of the same product. To achieve such environmental improvements, renewable energy must be used, particularly to produce hydrogen from water electrolysis. Importantly, different methodological choices are identified that are being used in the LCA studies, making results not comparable. There is a clear need to harmonize LCA methods for the analyses of CCU systems, and more importantly, to document and justify such methodological choices in the LCA report.

1. Introduction

Global anthropogenic fossil CO_2 emissions have continuously increased over the last decades, peaking at 37.9 Gt in 2018.[1] They represent over 75% of the total anthropogenic greenhouse gas (GHG) emissions,[1] causing global warming and therefore affecting the Earth's climate system. The Intergovernmental Panel on Climate Change (IPCC)[2] estimates that, if these emissions keep growing at the current rate, global warming is likely to reach 1.5 °C between 2030 and 2052. The Paris Agreement Work Programme, under the United Nations Framework Convention on Climate Change, aims to maintain the increase in global average temperature to below 2 °C, ideally below 1.5 °C, above pre-industrial levels.[3]

Most efforts to mitigate the effects of climate change have been directed towards reducing anthropogenic CO_2 emissions. Different approaches are being considered by improving the efficiency of different processes. Alternatively, there are opportunities to capture CO_2 that has been emitted, or would be emitted, to the atmosphere, preventing an increase of CO_2 concentration in the air. Such 'carbon capture' options include Carbon Capture and Storage (CCS), to permanently store CO_2 preventing its release to the atmosphere, and Carbon Capture and Utilization (CCU), to use the captured CO_2 in different industrial applications. Both CCS and CCU support a circular carbon economy where carbon emissions are reduced, reused, recycled and removed.

In fact, CCU continues to gain pace. Figure 1 shows the number of research papers published per year as identified by a Scopus search of the terms CCU and "CO_2 or carbon dioxide" or "carbon dioxide utili*ation" or " CO_2 recycling" or " CO_2 utili*ation" or "carbon capture and utili*ation" or "carbon dioxide recycling" or "carbon capture and recycling" or "carbon dioxide reactions" or "CO_2 conversion" or "carbon dioxide conversion". It can be seen that, since 2012, there has been a growth in the number of publications demonstrating an increase in research activity.

Although it has been claimed that CCU may play a role to both reduce dependency on fossil fuels and reach climate-change mitigation targets,[4] CCU's potential to reduce CO_2 emissions is very limited compared to that of CCS.[5,6] However, CCU has other advantages by providing valuable CO_2-based products,[7] enhancing resource scarcity and minimizing the use of fossil resources.[8] Numerous reports have discussed the potential of using CO_2 as an alternative carbon source within the chemical industry.[7,9,10] It has also been claimed that CCU has the potential to strengthen business models for further industrial emissions reduction.[11]

The International Energy Agency[7] identified five categories of such products: fuels, chemicals, building materials from minerals, building materials from waste and fertilizer of biological processes. The production of fuels could increase the demand of CO_2 by up to 2050 Mt per year,[12] or between 500 and 6200 Mt CO_2 per year in 2050 for CO_2-based fuels, chemicals and concrete building materials.[13] Other sources give a much higher estimation, with a potential of CO_2 used in

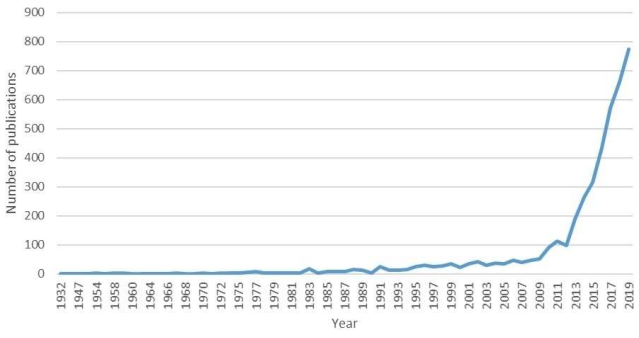


Figure 1. Number of publications on CCU in Scopus.

[a] *Dr. G. Garcia-Garcia, K. Armstrong, Prof. P. Styring*
UK Centre for CO_2 Utilization
Department of Chemical and Biological Engineering
The University of Sheffield
Sir Robert Hadfield Building, Sheffield, S1 3JD (UK)
E-mail: p.styring@sheffield.ac.uk
[b] *M. C. Fernandez, S. Woolass*
Tata Steel, Unit 2
Meadowhall Business Park
Carbrook Hall Road, Sheffield S9 2EQ (UK)

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

a circular carbon economy to be about 14 Gt CO_2 per year in 2050,[14] either temporarily or on a longer time scale.

The only way to make CO_2-based products competitive in the market is to ensure that they have associated economic and/or environmental benefits over the current manufacturing of these products, or to manufacture products with an improved performance over existing similar products. Since CO_2-based products are commonly the same as those they could substitute (they are chemically identical but are manufactured by a different reaction and from different raw materials), and generally CO_2-based products are still more expensive than the substituted products, the potential environmental benefits of the CO_2-based products may be the key factor that could make their manufacturing more favorable. Assessing such environmental impacts and benefits of CO_2-based products is challenging due to the amount of data and calculations required.

Life-Cycle Assessments (LCA) are needed to obtain reliable environmental results.[15] LCA is a widely used methodology to assess the environmental impacts of products in all their life-cycle stages and its use is increasing in both the research field and the industrial sector.[16] Due to its increasing popularity in the last twenty years, LCA has been standardized by the International Organization for Standardization.[17,18] Consequently, there is a clear need to undertake LCAs of CCU processes to quantify environmental impacts or benefits of these solutions.[19–23] Nevertheless, there is a lack of such studies.[5,24–27] Some CCU processes and products have not yet been studied. For others, such studies become quickly outdated, since research in the CCU field is rapidly evolving and providing novel, better solutions. In this context, we believe that an article that reviews and discusses all the published evidence of the life-cycle environmental impacts of the most promising CCU technologies, focusing on the most-recently published studies, would be a very valuable contribution to the CCU community. Furthermore, as the LCA methodology keeps constantly evolving too, a critical analysis of the LCA methodological decisions undertaken in CCU studies is also needed. Such analysis would clarify which products could be produced via CCU rather than by conventional methods, so their life-cycle environmental impacts can be reduced. Although some valuable tutorials and reviews have been published in the past on this area (e.g., von der Assen et al.[28] and Thonemann[29]), several key studies have been published since, some new developments have been achieved, and important CCU products have not yet been analyzed.

Peter Styring is Professor of Chemical Engineering & Chemistry at The University of Sheffield, UK. Peter's main research areas cover novel sorbents and processes for carbon dioxide capture and purification, processes for carbon dioxide utilization, including catalysts design, and techno-economic analysis of CDU processes. He is a Fellow of the Royal Society of Chemistry and the Institution of Chemical Engineers and a Chartered Engineer and Chemist. Peter is Director of the UK Centre for Carbon Dioxide Utilization and the CO2Chem Network and a member of the Scientific Advisory Board of the International Conference on Carbon Dioxide Utilization (ICCDU).

Based on these considerations, this article aims to analytically review the life-cycle environmental impacts of some of the most promising products that could be manufactured from CO_2, at an industrial scale in the short-medium term. The CO_2-based products selected for this study were methanol, methane, dimethyl ether (DME), dimethyl carbonate (DMC), propane and propene. We aimed to compare the key results for each product as well as the main methodological approaches used in the reviewed papers. This article is structured as follows: Section 2 describes the methodology used to undertake the review of the state of the art, Section 3 identifies the CO_2-based products to be analyzed, Section 4 assesses the environmental impact of these products, Section 5 discusses the use of LCA methodology to assess the environmental impacts of CCU, and Section 6 provides a summary of the main conclusions of the article.

2. Methodology

The objective of the analytical literature review is to identify and critically analyze the most relevant, up-to-date articles and reports on life-cycle environmental impacts of CCU routes to produce valuable chemicals. The review methodology used to achieve this aim consists of six stages, as shown in Figure 2. Five of these stages are based on the methodology followed by Stone and Rahimifard,[30] who, in turn, applied the methodology explained by Denyer and Tranfield.[31] The six stages of the review methodology are explained below.

2.1. Formulation of review questions

The formulation of review questions can aid to narrow down the scope of the analytical review and clarify what should be considered and excluded from the study. In order to review the life-cycle environmental impacts of CCU routes to produce valuable chemicals, the following questions must be answered:

1. What are the potential environmental impacts and/or benefits of producing these products from CO_2, in comparison with traditional methods?
2. To what extent has the LCA methodology been consistently used to study the environmental impacts of CCU?

Sections 3–5 aim to answer these questions from the findings of the analytical literature review.

2.2. Definition of a precise review scope

Answering the first review question from the previous section is necessary to define the precise scope of the analytical literature review, as it identifies the products and technologies to be

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Table 1. Generation of search strings by combination of three-level keywords.

Primary words (CCU related)	Secondary words (environment related)	Tertiary words (products)
"carbon capture and utili*"	environment*	methanol
"CO2 utili*"	"life cycle"	methane
CCU	emission*	dimethyl ether
"CO2-based"	greenhouse	dimethyl carbonate (and dimethylcarbonate)
		propane
		propene (and propylene)

Table 2. Number of papers found initially and remaining after each filter.

Criteria	Number of articles
total papers found	21440
unique papers found	5729
$\geq$2015 or $\geq$100 citations	5110
filter by number of citations	1977
SCImago journal ranking $\geq$1	1145
title/abstract screening	255

analysed in detail from an environmental perspective. Therefore, a preliminary, broad review of CCU products and processes was undertaken to identify such products and technologies, which were later considered in the comprehensive literature search (Section 2.3 and Table 1). This preliminary analysis was completed by a review of the most up-to-date, relevant, high-quality articles that analyse future prospects of CCU products and processes, along with the authors' knowledge in the subject and consultation with experts. The results of such preliminary analysis are summarised in Section 3.

2.3. Location of literature

Once the review scope was precisely defined in Stages 1 and 2, the most relevant literature was identified in Stage 3. To do so, a list of keywords relevant to the review scope was prepared. These keywords were classified into three categories, as shown in Table 1: words related to CCU, to the environment, and to CCU products (primary, secondary and tertiary words, respectively). The list of products (tertiary words) was shortlisted in Stage 2.2 and will be explained in more detail in Section 3. Since different synonyms and abbreviations are used in different articles, different terminologies were used to list keywords (e.g., "carbon capture and utili*" and "CCU"). However, this was not deemed necessary for the term "life cycle", because this is often followed by several different words, such as "assessment", "analysis", "study", "environmental impacts", and in the most common term (LCA, i.e., "life-cycle assessment"), the words "life cycle" should appear in the text the first time the abbreviation is used. Furthermore, the term "carbon capture" was not specific enough as this could refer to carbon capture and storage (CCS). The asterisk symbol * was used in the searches to find keywords with the same letters on the left of * (e.g., "utili*" would search for "utilisation" and "utilization", "environment*" would search for "environment" and "environmental"). Similarly, quotation marks "" were used to find specific phrases (e.g., "CO2 utilization", rather than "CO2" AND "utilization"). It must be noted that "CO2-based" shows results of both "CO2-based" and "CO2 based".

The keywords listed in Table 1 were used to create search strings in the following way: one primary word AND one secondary word AND one tertiary word. For instance, the following search strings were used for the first, secondary and tertiary words: "Carbon capture and utili*" AND Environment* AND Methanol. Consequently, 128 search strings were used in total. It must be noted that the same articles were frequently found by using different search strings. The search strings selected were used in online searches undertaken between November and January 2020, in Scopus. Some articles that were published after this period, and that were found while this article was being written, were also analyzed.

2.4. Selection and evaluation of relevant literature

A total of 21440 articles were found by the search strings described in the previous section. As the total number of papers found was too high to be manually screened, a number of steps were taken to reduce this list to the key papers. The number of papers left after each step is collected in Table 2. This process was undertaken by exporting the list generated in each search engine to an Excel spreadsheet, which allowed for an easier examination of the articles' information by displaying different fields and metadata in columns, and then using built-in Excel functions to search and organize data.

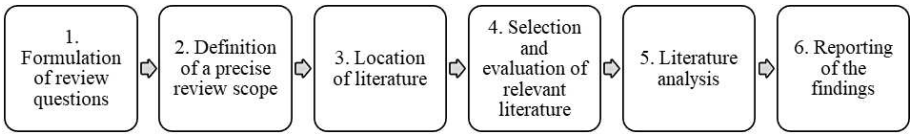


Figure 2. Methodology for analytical review, partially based on previous reviews.[30,31]

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Table 3. Filter by number of citations.

Publication year	Number of citations needed to pass filter
prior to 2015	100
2015	50
2016	40
2017	30
2018	20
2019	10
2020	0

During the different searches, a number of articles appeared multiple times, so duplicates were removed. In order to find the most relevant and updated articles in the subject, articles published in the last six years were prioritized (2015–2020). However, there were a number of relevant articles published prior to 2015 that should be considered, so articles with a number of citations larger than 100 were included regardless of the year of publication. Due to the recent growth in the CCU field, and particularly the increased application of LCA and environmental impact studies to this field, most relevant articles in this field were published after 2015 nonetheless, since, as noted by von der Assen,[32] LCA was not standard practice for environmental studies of CCU before 2014.

In order to reduce the list of papers further, this list was scrutinized to remove articles that did not meet the following criteria, regarding the number of citations and the publication year as shown in Table 3.

The articles must have been written in English language, have been accessible online and have been peer reviewed (except grey literature from prestigious organizations). Articles published in a journal with an SCImago journal ranking (SJR) equal or higher than 1 were considered further. SJR is a numeric value indicating the relative impact of the journal where the article is published. It is calculated by the number of citations that journal has, and the importance of the journals where those citations originated from.

The remaining articles were filtered on the basis of title and abstract content. Within the field of CCU there are not only many technology options, but a significant amount of catalysts for each process. Many of the articles referred to the synthesis and tailoring of the catalysts for the reactions, with no mention of the environmental impact or were not directly related to the research questions.

The analysis described in this subsection reduced the initial search pool from the initial 21440 articles to a refined 255 articles.

2.5. Literature analysis

In this stage, the final list of 255 articles generated from the previous stages was closely analyzed to find the answers to the questions listed in Section 2.1. A detailed read of each of the articles was used to identify and extract the most relevant information.

2.6. Reporting of the findings

In this final stage, the findings from the literature analysis were reported, as well as the extent to which the collected findings have addressed the research questions from Section 2.1. These findings, structured in three sections addressing one research question each, are reported in the next sections.

3. Production of Valuable Products from CO_2

There is a wide range of products that can be produced from CO_2, such as fuels, chemicals and building materials. This section aims firstly to identify the most common CO_2-based products currently manufactured in the industry, to then focus on the CO_2-based products considered in the scope of this article: methanol, methane, DME, DMC, propane and propene. Additionally, the technologies needed to manufacture such products by current, standard methods are identified in this section.

Out of the current 230 Mt of CO_2 consumed per year, 130 Mt are used to manufacture urea, 70–80 Mt to support enhanced oil recovery operations, around 14 Mt are used in the food and drinks sector, while the rest is used in applications such as fabrication of metal, cooling, fire suppression and in greenhouses to stimulate plant growth.[7] The production of urea, an important fertilizer, is produced commercially by reacting ammonia and CO_2 via the Bosch-Meiser process, developed in 1922.[33]

Recent research has enabled the production of a number of new CO_2-based products. Since these products are currently produced by traditional methods that have been optimized over time, CO_2-based products are not often economically profitable. Chauvy et al.[34] applied a multi-criteria assessment to classify viable emerging CO_2-based products according to technical, economic, energetic, environmental and market considerations. This assessment was based on the Analytical Hierarchy Process (AHP) method, qualitative uncertainty analysis and sensitivity analysis. Their results show that the most promising CO_2-based products, suitable for short-term implementation, are methanol, DMC and methane. This is, for methanol and methane, because of the maturity of their manufacturing technology, size of the market potential and the applicability of the products. DMC, on the other hand, is a highly valuable chemical and its production from CO_2 seems to be less toxic than its conventional manufacturing. For these three products, their manufacturing, starting from CO_2 as a raw material, could be commercialized in less than five years, with a current Technology Readiness Level (TRL) of 7–9.[34–36] TRLs are scales widely used by the industry to assess maturity of different technologies and enable comparison between them.[37] They range from 1 (observation of basic principles) to 9 (demonstration in operational environment).

DME can be used as a clean fuel, substituting diesel and as a valuable intermediate in the petrochemical industry.[38] Its manufacturing from CO_2, although expensive due to high electricity costs, has been proven as technically feasible, which

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Table 4. Main processes to manufacture the shortlisted products.

Product	Current standard process	Ref.
methanol	hydrogenation of carbon monoxide (from syngas)	[45]
methane	hydrogenation of carbon dioxide (Sabatier reaction)	[46]
DME	methanol dehydration from syngas	[47]
DMC	reaction of phosgene	[48]
propane	production from natural gas or oil refining	[49]
propene	steam cracking of naphtha and gas oils	[50]

is promising due to the projected increase of DME market value and demand.[39] Propane is a fuel currently used for heating, cooking and transportation. Its market was estimated at 195 Mt in 2016 and is expected to keep growing.[40] Propane can be produced from CO_2 via methanol synthesis.[41,42] Propene (also known as propylene) is used as a feedstock to produce a variety of chemicals, including polypropylene, propylene oxide and acrylonitrile. Propene manufacturing from CO_2 and H_2 has already been investigated.[43] The CarbonNext project[44] also identified propene, methanol, methane and DME (along with other six chemicals) as the best suited chemicals to be produced from CO_2 and therefore replace fossil sources, based on their TRL, market value, CO_2 utilization potential and not requiring of other non-catalytic chemical inputs that contain fossil carbon.

Table 4 shows, for each of the six aforementioned products, the standard, most common processes currently used for their industrial manufacturing. The environmental impact associated to these processes to produce the shortlisted products, is assessed in Section 4.

The distribution of papers screened according to the publication year is shown in Figure 3. The number of relevant publications has generally increased over the years. This article was written in early 2020, so only a few articles published in 2020 were found and registered within this review.

A thorough analysis of the papers found, revealed that from the 255 screened papers, 103 were not relevant (i.e., did not report on environmental impacts of the CCU products). The distribution of products studied in the papers can be seen in Figure 4. The main product studied in the literature examined is methanol, followed by methane and fuels, hydrocarbons and lower olefins. The need for hydrogen has been found as a hotspot in many carbon capture and utilization processes, and

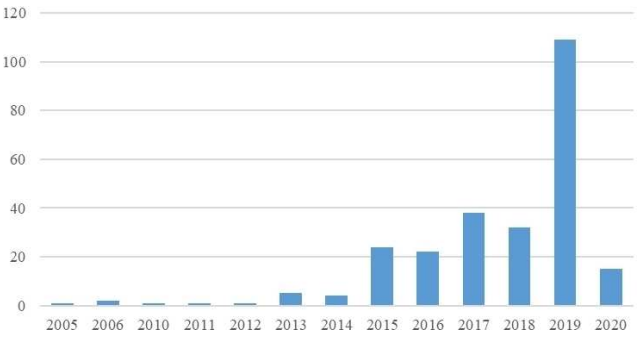


Figure 3. Number of publications per year.

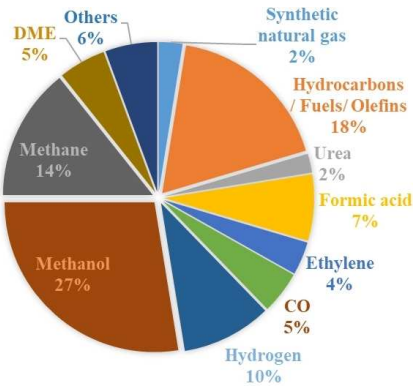


Figure 4. Product focus distribution within the screened papers.

as a result, a number of papers focus upon the generation of hydrogen. A small fraction of the papers made no reference to a particular product or referred to different aspects of LCA. When a paper studied more than one product, it has been included in each product's chart fraction.

4. Environmental Impacts and Benefits of Producing the Identified Products from CO_2

In general, CCU routes to produce a chemical are considered more environmentally friendly than conventional technologies, since CCU utilizes CO_2 that would otherwise be in the atmosphere (consequently, the global warming impact may be reduced), and it uses CO_2 instead of fossil resources as a raw material (therefore, the resources depletion impact may be reduced). This is illustrated in Figure 5, where the process gas from a point source containing CO_2 becomes the feedstock for the CCU plant. The production of the chemical from CO_2 displaces the use of fossil sources within the chemical industry and reduces the emissions of CO_2 from the point source.

However, even if the global warming and resources depletion impacts are reduced by implementing a CCU technology, the environmental impact of other impact categories may increase, for instance, ecotoxicity, acidification, or

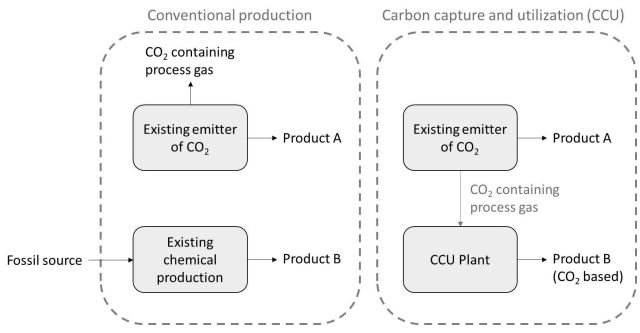


Figure 5. Basic comparison between conventional and CCU production.

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

ionizing radiation (namely, "burden shifting"). Furthermore, CO_2 emissions and resource use may also increase with CCU solutions since these options generally need a significant amount of energy to capture CO_2 and then transform it to the final product.

For instance, the energy requirement of capturing CO_2, known as energy penalty, is often significant, and depends on the capture technology used and the point sources (i.e., where CO_2 is captured from). Currently, the additional energy input per t of CO_2 captured is higher for natural gas power plants than for coal power plants, but the CO_2 penalty is considerably lower for natural gas power plants. This is due to the lower specific CO_2 emissions of natural gas combustion.[51–53] Carbon capture from refinery processes requires the least additional primary energy, and when related to natural gas, the CO_2 penalty is considerably lower than for cement or iron and steel production. Cement production has the highest additional energy input per CO_2 captured, and as coal is primarily utilized, the CO_2 penalty is considerably higher than for the other evaluated processes.[51,54] Once CO_2 has been captured, its activation is key to achieve an environmentally friendly (and economically feasible) CCU process.[55]

Therefore, energy requirements continue to remain a key issue in CCU, as energy for CO_2 utilisation must come from low-carbon sources to ensure minimal environmental impacts. Kätelhön et al. calculated that 55% of the global energy production in 2030, that is, more than 18 PWh, would be required to realise the potential of CO_2 utilisation.[56] And herein lies a conundrum for CO_2 utilisation matching the potential to create low-carbon chemicals with the vast amount of low-carbon energy that this would require. To reduce the energy requirement, the SCOT project[57] identified key technical research and innovation challenges such as catalysis, reactor design, separation techniques and novel reaction pathways.

To consider the aforementioned aspects and evaluate life-cycle environmental impacts in a systematic manner, it is important to use an LCA methodology, as this allows analyzing environmental impacts of CCU technologies, considering a wide range of environmental impacts, and all relevant processes and stages of the supply chain. The next subsections show the reported environmental impacts of producing the chemicals identified in Section 3 via both conventional and CCU methods, with a focus on LCA studies and considerations.

4.1. Methanol

Methanol can be used as a fuel, for example, for internal combustion engines, fuel cells and stoves. Due to its high-octane rating, it is a good additive or substitute for gasoline in internal combustion engines.[58,59] With cleaner burning properties than regular gasoline, it reduces the emission of other pollutants as well. Recent studies demonstrate an interest on the use of alcohols, such as methanol, as fuel in sectors difficult to decarbonize, like maritime[60] and aviation.[61] Methanol can be transformed into ethene, propene, formaldehyde, acetic acid and other products usually derived from petrochemicals. Through the methanol-to-olefins process, it can produce light olefins like ethene and propene, commonly used to make polymers.

Methanol is traditionally produced by the hydrogenation of carbon monoxide, where pressurized synthesis gas (syngas) reacts in the presence of a catalyst. Syngas can be produced either by steam reforming in the case of light hydrocarbons, such as natural gas or light naphthas, or by partial oxidation, in the case of heavy oils or solid carbonaceous materials. Typical CO_2 emissions from methanol production range between 0.5 $t_{CO_2\ eq}\ t_{methanol}^{-1}$ for steam reforming with primary reform and 1.4 $t_{CO_2\ eq}\ t_{methanol}^{-1}$ for partial oxidation of residual oil (Table 5).[62] In Europe, due to the use of both technologies, the average CO_2 emissions (direct and indirect) are assumed to be 0.76 $t_{CO_2\ eq}\ t_{methanol}^{-1}$.[63] Artz et al. reviewed LCA studies on methanol and provided a more recent and narrower estimated range of the global warming impact of methanol produced by fossil-based processes of 0.68–1.08 $t_{CO_2\ eq}\ t_{methanol}^{-1}$.[64]

Methanol produced with renewable energy, water and CO_2 has been described as one of the most promising future fuel options.[65–72] A successful example is the work carried out by Khanipour et al.,[73] who proposed a new configuration of a flare gas treatment to collect hydrogen and CO_2 that is subsequently reacted to produce methanol. They estimated that this allowed avoiding the emission of 300 t_{CO_2} per day.

It has been estimated that the net CO_2 emissions for a plant producing methanol from the hydrogenation of captured CO_2 are 0.23 $t_{CO_2}\ t_{methanol}^{-1}$[63] (lower than the average emissions of European methanol plants of 0.76 $t_{CO_2}\ t_{methanol}^{-1}$). Moreover, since the discussed hydrogenation process utilizes up to 1.4 $t_{CO_2}\ t_{methanol}^{-1}$, the net amount of CO_2 avoided, compared to the current average emissions, is in the region of 2 $t_{CO_2}\ t_{methanol}^{-1}$.[63] According to this study, the yearly direct and indirect gate-to-gate emissions of the CCU process to produce methanol was 0.1 Mt y^{-1}, while a conventional plant to synthesize methanol emits 1.7 Mt y^{-1}. The CO_2 not produced, defined as the difference between the CO_2 emissions of the conventional route compared to the CCU route, was 0.54 $t_{CO_2}\ t_{methanol}^{-1}$. The CO_2 avoided, defined as the difference between the CO_2 not produced and the CO_2 that enters the CCU plant as a raw material to be used, was 2 $t_{CO_2}\ t_{methanol}^{-1}$. However, this study considered that the hydrogen required to synthesize methanol was provided by a hydrogen network that was outside of the boundaries of their study. If full life-cycle emissions are considered, hydrogen production must be taken into account, and this would significantly impact the overall CO_2 emissions reductions. Considering the methanol production volume in 2011 in the European Union, CO_2-based methanol could avoid the emission of nearly 4 Mt of CO_2 per year.[74]

Nguyen and Zondervan[75] compared the CO_2 emissions of methanol production by hydrogenation, bi-reforming and tri-reforming of CO_2. Both direct (from flue gases) and indirect emissions (from steam and electricity generation, from hydrogen and oxygen production and from the natural gas supply chain) were considered. For a methanol plant with capacity of 3500 t day^{-1}, CO_2 hydrogenation with hydrogen from steam reforming showed the highest CO_2 emissions (1.47 $t_{CO_2}\ t_{methanol}^{-1}$)

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Table 5. CO_2 emissions of different methods to produce methanol.

Technology/ process	System boundaries	Hydrogen and electricity source	CO_2 emissions	Notes	Ref.
steam reforming with primary reform	cradle-to-gate		0.5 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	standard production (non-CCU)	[87]
partial oxidation of residual oil	cradle-to-gate		1.4 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	standard production (non-CCU)	[87]
steam reforming of natural gas	cradle-to-gate		0.85 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	standard production (non-CCU); includes emissions associated to production and transport of natural gas	[43]
steam reforming of natural gas	cradle-to-gate; construction, fuel production, and disassembly of the production plant is included; utilities (heat and electricity) are included		0.67 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	standard production (non-CCU)	[88]
steam reforming or partial oxidation	cradle-to-gate		0.68–1.08 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	standard production (non-CCU)	[64]
hydrogenation of CO_2, Cu/ZnO/Al_2O_3 catalyst	cradle-to-gate	various	1.21–1.44 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	values for several reviewed studies	[64]
hydrogenation of CO_2, Cu/ZnO/Al_2O_3 catalyst	gate-to-gate, including CO_2 capture and conversion, hydrogen production, infrastructure; excluding transport, storage, and recovery and reuse of catalyst	wind-based electricity for water electrolysis, European energetic mix ENTSO–E for CO_2 capture and conversion	0.226 $t_{CO_2\ eq}\ t_{methanol}^{-1}$ (indirect + direct)	includes the utilization of 1.6 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock; CO_2 captured with MEA from a conventional cement plant; an allocation of CO_2 emissions from cement plant (clinker production) is included	[78]
hydrogenation of CO_2, Cu/ZnO/Al_2O_3 catalyst	gate-to-gate, excluding hydrogen generation and carbon capture	hydrogen generation not included, electricity use (for compression and pumping) from conventional pulverised coal power plant; 0.17 MWh t^{-1} for electricity requirements to produce methanol	0.13 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	does not include the utilization of −1.46 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[63]
hydrogenation of CO_2, Cu/ZnO/Al_2O_3 catalyst	emissions from flue gases, steam and electricity generation, hydrogen and oxygen production and the natural gas supply chain were considered	electricity from natural gas, hydrogen from steam reforming	2.983 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	average for three plant capacities (300, 1500, and 3500 t day^{-1}); does not include the utilization of −1.54 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[75]
hydrogenation of CO_2, Cu/ZnO/Al_2O_3 catalyst	emissions from flue gases, steam and electricity generation, hydrogen and oxygen production and the natural gas supply chain were considered	electricity from natural gas, hydrogen from wind-powered electrolysis	0.657 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	average for three plant capacities (300, 1500, and 3500 t day^{-1}); does not include the utilization of −1.54 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[75]
hydrogenation of CO_2, Cu/ZnO/Al_2O_3 catalyst	emissions from flue gases, steam and electricity generation, hydrogen and oxygen production and the natural gas supply chain were considered	electricity from natural gas, hydrogen from reforming of biomethane from wood	1.958 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	average for three plant capacities (300, 1500, and 3500 t day^{-1}); does not include the utilization of −1.54 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[75]
hydrogenation of CO_2, Cu/ZnO/Al_2O_3 catalyst	emissions from flue gases, steam and electricity generation, hydrogen and oxygen production and the natural gas supply chain were considered	electricity from natural gas, hydrogen from biomass gasification	1.110 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	average for three plant capacities (300, 1500, and 3500 t day^{-1}); does not include the utilization of −1.54 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[75]
hydrogenation of CO_2, Cu/ZnO/Al_2O_3 catalyst	emissions from flue gases, steam and electricity generation, hydrogen and oxygen production and the natural gas supply chain were considered	electricity from natural gas, hydrogen from solar-powered electrolysis	1.508 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	average for three plant capacities (300, 1500, and 3500 t day^{-1}); does not include the utilization of −1.54 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[75]
hydrogenation of CO_2, Cu/ZnO/Al_2O_3 catalyst	emissions from flue gases, steam and electricity generation, hydrogen and oxygen production and the natural	electricity from natural gas, hydrogen from hydro-powered electrolysis	0.899 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	average for three plant capacities (300, 1500, and 3500 t day^{-1}); does not include the utilization of −1.54 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[75]

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Table 5. continued

Technology/ process	System boundaries	Hydrogen and electricity source	CO_2 emissions	Notes	Ref.
	gas supply chain were considered				
bi-reforming	emissions from flue gases, steam and electricity generation, hydrogen and oxygen production and the natural gas supply chain were considered	electricity from natural gas	1.768 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	average for three plant capacities (300, 1500, and 3500 t day^{-1}); does not include the utilization of −0.36 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[75]
tri-reforming	emissions from flue gases, steam and electricity generation, hydrogen and oxygen production and the natural gas supply chain were considered	electricity from natural gas, oxygen from cryogenic air-distillation	1.726 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	average for three plant capacities (300, 1500, and 3500 t day^{-1}); does not include the utilization of −0.36 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[75]
tri-reforming	emissions from flue gases, steam and electricity generation, hydrogen and oxygen production and the natural gas supply chain were considered	electricity from natural gas, oxygen from water electrolysis	1.763 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	average for three plant capacities (300, 1500, and 3500 t day^{-1}); does not include the utilization of −0.36 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock	[75]
steam reforming of natural gas	cradle-to-gate; utilities (electricity, heat and water) are included; distribution is excluded	electricity from European grid mix	0.525 $t_{CO_2\ eq}\ t_{methanol}^{-1}$ (from ecoinvent 3)	standard production (non-CCU)	[77]
electrochemical reduction of CO_2 with water	cradle-to-gate; utilities (electricity, heat and water) are included; distribution is excluded	electricity from photovoltaic panels; no hydrogen used	949 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	assumed feedstock CO_2 free of environmental burdens	[77]
hydrogenation of CO_2	process-related emissions only	hydrogen from water electrolysis powered by wind electricity	0.123 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	does not include the utilization of 1.37 $t_{CO_2}\ t_{methanol}^{-1}$ as feedstock, nor the emission associated to the CO_2 source (0.58 $t_{CO_2}\ t_{methanol}^{-1}$)	[43]
reduction of CO_2 to CO, water gas shift and methanol synthesis	cradle-to-gate; construction, fuel production, and disassembly of the production plant is included; utilities (heat and electricity) are included	hydrogen generated on site via water gas shift, heat and electricity generated from conventional fuels	1.87 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	includes the utilization of CO_2 as feedstock	[88]
reduction of CO_2 to CO, water gas shift and methanol synthesis	cradle-to-gate; construction, fuel production, and disassembly of the production plant is included; utilities (heat and electricity) are included	hydrogen generated on site via water gas shift, heat and electricity generated from solar energy	-1.70 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	includes the utilization of CO_2 as feedstock	[88]
hydrogenation of CO_2	cradle-to-gate	electricity from the German grid mix, hydrogen from polymer electrolyte membrane electrolysis	6.27 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [78,79, 89–94])
hydrogenation of CO_2	cradle-to-gate	electricity from wind energy, hydrogen from polymer electrolyte membrane electrolysis	-0.87 $t_{CO_2\ eq}\ t_{methanol}^{-1}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [78,79, 89–95])
hydrogenation of CO_2	cradle-to-gate	hydrogen from electrolysis powered by wind energy	0.3 $t_{CO_2\ eq}\ MJ_{methanol}^{-1}$	CO_2 captured from biomass fermentation	[96]
electrochemical methanol production	gate-to-gate	carbon neutral renewable energy input	$1.74 \cdot 10^{-6}\ t_{CO_2\ eq}\ MJ^{-1}$	CO_2 captured does not have an allocated impact	[83]
hydrogenation of CO_2 using solar energy	cradle-to-gate	considers utilities from solar energy or conventional fuels	normalised results against reference (100%); 278% larger GWP when using conventional fuels and −253% when using solar energy	the construction of the methanol plant is also considered separately, at 1.87 $kg_{CO_2\ eq}\ kg_{methanol}^{-1}$ for utilities from conventional fuels and −1.71 $kg_{CO_2\ eq}\ kg_{methanol}^{-1}$ using solar energy	[79]

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

due to the hydrogen production. Tri-reforming processes performed slightly better than bi-reforming. Hydrogenation with solar, biomass, hydropower and wind achieved negative CO_2 emissions. Wind-powered hydrogenation showed the lowest CO_2 emissions, with -0.86 t_{CO_2} $t^{-1}_{methanol}$. All technologies considered in the study reduced CO_2 emissions compared to a typical industrial methanol plant (1.5–1.9 t_{CO_2} $t^{-1}_{methanol}$, according to this study, higher than current average European emissions).

Milani et al.[76] modelled the integration of CO_2 captured from a power plant into an existing methanol plant fed with natural gas, in order to produce CO_2-based methanol. Results showed that this integration achieved a combined reduction in CO_2 emissions of 21.9% for both the power plant and the methanol plant, which corresponds to 502 t_{CO_2} h^{-1}.

In contrast with the previous studies, Abanades et al.[24] compared the CO_2 mitigation potential of a CCU system powered with renewable energy producing methanol (taken from Pérez-Fortes et al.[63]) to the conventional methanol production from fossil fuels, and concluded that the CCU system did not perform better with regard to climate change impact. The authors also estimated that a CCS option using renewable electricity is significantly more effective at reducing CO_2 emissions than the CCU system.

Rumayor et al.[77] compared the carbon footprint for the production of methanol by the conventional natural gas route, via direct hydrogenation of CO_2 and via electrochemical reduction of CO_2. The electrochemical reduction of CO_2 showed much higher CO_2 emissions than direct hydrogenation due to the large need for steam for heating in the distillation process. In what the authors labelled as "ideal conditions" and including the amount of CO_2 used to produce the methanol, these emissions could be significantly reduced and become even smaller to those of the conventional process.

Meunier et al.[78] reported a reduction of 1.3 $t_{CO_2\ eq}$ $t^{-1}_{methanol}$ for an integrated CO_2 based process in comparison to 2.8 $t_{CO_2\ eq}$ $t^{-1}_{methanol}$ for the reference system based on the CO_2 emissions from cement plant without CO_2 capture and from the conventional process for the production of methanol from steam methane reforming of natural gas. Similar results were achieved by other authors,[79–81] when comparing traditional methanol production via natural gas and the utilization of CO_2 from flue gases combined with solar energy for the production of methanol. All "sunshine-to-petrol" processes showed negative global warming potential scores compared to a conventional natural gas-based route. In fact, solar energy can be used to perform electrolysis of water, or perform photoelectrochemical water splitting via a thermochemical route, in both cases generating hydrogen for compression and further uses for methanol synthesis.[82]

Well-to-wheel LCAs can be used to compare environmental impacts of different fuels, considering the extraction of materials, the production of the fuel, its distribution to the vehicle, and the utilization of the fuel in the vehicle. The well-to-wheel CO_2 emissions of methanol from CO_2 recycling and hydrogen from renewable sources were estimated at 1.74 $g_{CO_2\ eq}$ MJ^{-1}, significantly smaller than the reference fossil fuel emission of 83.8 $g_{CO_2\ eq}$ MJ^{-1} chosen as the comparator by the EU Fuel Quality Directive for biofuels.[83] This study estimated that the well-to-wheel GHG emissions of CO_2-methanol produced with renewable energy were reduced by 98% compared to gasoline and diesel.

The electricity requirements for the reaction to produce methanol by CO_2 hydrogenation are usually large. They have been estimated to be 0.17 MWh $t^{-1}_{methanol}$.[63] However, this figure excludes the hydrogen production and the carbon capture process. Furthermore, in order to maintain a negative CO_2 balance for the process, it is imperative that a renewable source of electricity is used. More than 80% of the energy needed to produce methanol from CO_2 is required to produce renewable hydrogen, whilst around 10% is needed to capture CO_2 from a fossil-fired power station.[6] If CO_2 is captured from air instead, the energy required for the process would increase from 43–44 GJ $t^{-1}_{methanol}$ [with an energy return on energy invested (EROEI) of 0.45] to around 60 GJ $t^{-1}_{methanol}$ (with an EROEI = 0.33).[6] These EROEI values are too low compared to those of mature energy-supplying technologies. Because of this low energy density and high energy required to produce CO_2-based methanol, this product could be more useful as a feedstock in the chemical industry, rather than as an energy carrier. These numbers are similar to those provided by Parra et al.,[27] who concluded that more than 90% of the life-cycle environmental impact of fossil-free hydrogen production is caused by the electricity supply for the electrolysis process. Koj et al.,[84] in their analysis of 32 LCA studies on Power-to-X, also concluded that the choice of electricity source, from renewable or fossil sources, affects the environmental performance of the process to a great degree.

It has been estimated that if renewable electricity is used for water electrolysis, CO_2-based methanol has a lower global warming impact than fossil-based methanol.[64,85] However, the global warming impact is higher if electrolysis is undertaken with fossil-based electricity (particularly coal) or if hydrogen is supplied by steam methane reforming of natural gas. It was estimated that, in a 2020 scenario, the global warming impact would be 1.21–1.44 $t_{CO_2\ eq}$ $t^{-1}_{methanol}$ (slightly higher than current fossil-based production), but this could be lowered to between -1.2 and -1.3 $t_{CO_2\ eq}$ $t^{-1}_{methanol}$ in a best-case scenario (with wind energy) via syngas generation and conventional synthesis or direct hydrogenation.[64] Bazzanella and Ausfelder[43] estimated that this CO_2-based methanol from water electrolysis powered by renewable energy could reduce emissions by 1.53 t_{CO_2} $t^{-1}_{methanol}$.

For other environmental impact categories, the hydrogen supply is still one of the main contributors to the overall environmental impact. In a study that considered wind energy-based water electrolysis, the environmental impact of hydrogen supply represented 59% of the impact of climate change, 41% of fossil depletion and almost 70% of water depletion.[78] The compression of the hydrogen and CO_2 also represents a significant impact in multiple environmental impact categories. The authors also considered the impact of performing a water and heat integration onsite between the CO_2 capture and conversion units, achieving a reduction of 2–24% of the environmental impacts. Particularly, the environmental impacts

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

on climate change and fossil depletion were reduced by 17 and 23% respectively.

Although the environmental impacts of the CO_2-based process are generally lower than the conventional methanol production, mineral depletion and water depletion, which are more related to the production of hydrogen, are exceptions, with an increase by 9 and 45% respectively.[78] For other environmental impacts, values were reduced by 77% for fossil resource depletion, 50% for human toxicity, 9% for freshwater eutrophication and 24% for terrestrial acidification. These results contrasts with values provided by Thonemann,[29] who estimated that results for all environmental impact categories would be worsened via CCU compared to the conventional scenario. This is particularly relevant for freshwater eutrophication and ionizing radiation using electricity from the grid, and freshwater ecotoxicity using wind electricity. In this second scenario, some environmental impact categories, such as ionizing radiation and ozone layer depletion, are slightly better for the CCU method.

With regard to the capture of CO_2, Meunier et al. carried out an LCA of a CO_2 capture unit in a cement plant for the production of methanol.[78] Within the CO_2 capture unit, the heat demand for the regeneration of the monoethanolamine (MEA) solvent contributed to 76 and 97% of the climate change impact and fossil resource depletion impact, respectively. As a result, it appears to be the most impacting demand in comparison to the use of electricity, water consumption and MEA production. The use of this solvent still presents a high-energy penalty for its regeneration and could also degrade the equipment due to corrosion issues. The remaining treated gas from the absorber also has an environmental impact and contributes to 52% of the terrestrial acidification.

The first modern commercial CO_2 to methanol recycling plant using locally available, cheap geothermal energy was set up by Carbon Recycling International (CRI) in Grindavik, Iceland. It is a demonstration plant, with an initial annual capacity of 4 kt methanol, that was increased up to 50000 L of liquid fuel per year. The produced methanol, called "Vulcanol", is currently mixed with gasoline. It is claimed they reduce greenhouse gas emissions by approximately 75% compared to conventional fuel.[86] Hydrogen is produced by water electrolysis using electricity produced from geothermal energy. In Japan, Mitsui chemicals has announced the planned construction of a demonstration plant, with a capacity of 100 t $year^{-1}$ to produce methanol, using CO_2 obtained as an industrial by-product and hydrogen generated by photochemical splitting of water using solar energy.[83]

In conclusion, methanol produced via CCU may reduce CO_2 emissions compared to conventionally produced methanol, but only if renewable energy is used, particularly to produce hydrogen. Results for other environmental impact categories are not clear, with some studies reporting larger impacts, while other analyses report smaller impacts. Particularly, water depletion, associated with hydrogen production, seems to be larger for the CCU method. Methanol is one of the CCU products that has been more widely investigated.

4.2. Methane

Methane is primarily used as a source of energy,[97] but can also be used as a raw material to produce biodiesel, methanol and other valuable hydrocarbons.[46] Methanation, the process by which methane is synthetized, is a relatively simple and fast reaction that generates methane under atmospheric pressure.[46] Multiple synergies exist in the production of methane by anaerobic digestion and the Sabatier reaction. The same infrastructure (e.g., for compression, transport and distribution) can be used for biomethane and synthetic methane. The methanation process is exothermic and the produced heat can be used elsewhere, for instance in the CO_2 capture process.[98]

Methane can be produced from CO_2 emitted from power plants and other emission point sources. The Power-to-Gas (CO_2 methanation) process has an estimated utilization of 1 t_{CO_2} t^{-1} of synthetic natural gas (SNG).[98] However, this figure considers the use of carbon-neutral hydrogen.[99] The electricity requirements for this process are 15.2 MWh t_{SNG}^{-1},[100] which must be met by a renewable and carbon-neutral source if the environmental impacts of the process are to be minimized. Bongartz et al.[101] estimated cradle-to-grave emissions of methane produced from CO_2 to be 14.1 $g_{CO_2\ eq}$ MJ^{-1} fuel. This value is lower than for current natural gas production and combustion (2.9 $t_{CO_2\ eq}$ t^{-1}, or 64 $g_{CO_2\ eq}$ t^{-1}).[102]

Therefore, the electricity source for hydrogen production significantly influences the global warming impact of producing methane from CO_2.[64] Using wind power for electrolysis has been associated a lower global warming impact than fossil-based production, even negative, in most studies (−0.04–0 $t_{CO_2\ eq}$ $t_{methane}^{-1}$).[89,90,103] In general, Safari and Dincer[88] recommend proton exchange membrane electrolysis (PEM) over the traditional electrolysis with KOH as electrolyte to produce hydrogen from water, due to its superior environmental performance, as well as lower maintenance costs. However, any hydrogen source other than water electrolysis powered with renewable energy generates a larger global warming impact (0–0.3 $t_{CO_2\ eq}$ $t_{methane}^{-1}$) than current fossil-based methane production ($\approx$0.1 $t_{CO_2\ eq}$ $t_{methane}^{-1}$).[91,104,105]

According to calculations by Reiter and Lindorfer,[104] process emissions lower than 113 g_{CO_2} kWh^{-1} (if CO_2 is considered a waste product) or 73 g_{CO_2} kWh^{-1} (if CO_2 separation is considered) in a Power-to-Methane process make it more competitive than conventional production (Table 6). Nevertheless, their assessment shows several weaknesses, such as omitting several aspects of the use of the product gas and infrastructure in the system boundaries, and lack of focus on multi-functionality issues.[103]

Parra et al.[27] calculated the life-cycle environmental impacts of SNG from Power-to-Methane and concluded that the impacts were higher than those from conventional natural gas in Switzerland, due to the large impact of the electrolysis process (which is powered in this example by renewable and non-renewable sources, as per the current Swiss electricity market). Only when all energy for the electrolysis is provided by renewable sources, environmental benefits are obtained. Furthermore, the environmental impact of the Power-to-Methane

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Table 6. CO_2 emissions of different methods to produce methane.

Technology/process	System boundaries	Hydrogen and electricity source	CO_2 emissions	Notes	Ref.
methane from fossil sources	cradle-to-gate		0.15 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	standard production (non-CCU)	[64]
methane from fossil sources			0.54 $kg_{CO_2\ eq}\ kg^{-1}_{CH_4}$	standard production (non-CCU)	[29]
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with wind power	−0.04 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from a cement plant, heat integration of the methanation with the capture process included, credit for utilized CO_2 is included	[64] (based on [89])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with wind power	−0.03 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from biogas, heat integration of the methanation with the capture process included, credit for utilized CO_2 is included	[64] (based on [89])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with wind power	−0.03 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from combustion of fossil fuels, heat integration of the methanation with the capture process included, credit for utilized CO_2 is included	[64] (based on [89])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with wind power	−0.02 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from direct air capture, heat integration of the methanation with the capture process included, credit for utilized CO_2 is included	[64] (based on [89])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with wind power, surplus energy	−0.002 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from combustion of fossil fuels, heat integration of the methanation with the capture process not included	[64] (based on [90])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with wind power	0.003 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from combustion of fossil fuels, energy requirements for compression and cooling of the reactor not included, no credit for utilized CO_2 is included	[64] (based on [27,103])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with photovoltaic power	0.002 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from combustion of fossil fuels, energy requirements for compression and cooling of the reactor not included, no credit for utilized CO_2 is included	[64] (based on [27,103])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with wind power	0.03 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from combustion of fossil fuels, no credit for utilized CO_2 is included	[64] (based on [104])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with photovoltaic power	0.06 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from combustion of fossil fuels, no credit for utilized CO_2 is included	[64] (based on [104])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with current EU grid mix	0.30 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from combustion of fossil fuels, no credit for utilized CO_2 is included	[64] (based on [104])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from steam methane reforming	0.09 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from combustion of fossil fuels	[64] (based on [91])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	hydrogen from electrolysis with EU grid mix 2020	0.21 $kg_{CO_2\ eq}\ MJ^{-1}_{CH_4}$	CO_2 from combustion of fossil fuels	[64] (based on [105])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	electricity from the German grid mix, hydrogen from polymer electrolyte membrane electrolysis	16.7 $kg_{CO_2\ eq}\ kg^{-1}_{CH_4}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [89–91,95, 104,105,109])
Sabatier reaction, nickel-based catalyst	cradle-to-gate	electricity from wind energy, hydrogen from polymer electrolyte membrane electrolysis	−1.99 $kg_{CO_2\ eq}\ kg^{-1}_{CH_4}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [89–91,95, 104,105,109])

system is slightly higher when CO_2 captured from air is used as opposed to CO_2 from biogas upgrade, since CO_2 from biogas upgrade is considered a waste product with no environmental burden (burden-free or cut-off approach). Although this cut-off approach is often recommended for CCU,[106] it is still important to consider the environmental impact of the capture process, as noted by Zhang et al.[103]

Zhang et al.[103] also applied the LCA methodology to study the environmental impacts of Power-to-Methane from different CO_2 sources and concluded that the climate change impact is reduced if compared to that of conventional natural gas for use as transport fuel. However, the normalised results of the LCA showed that the change in climate change impact is negligible compared to that of other environmental impact categories, particularly human toxicity (cancer effects); freshwater ecotoxicity; mineral, fossil and renewable resource depletion; and human toxicity (non-cancer effects). For all these categories, Power-to-Methane has a higher environmental impact than that of conventional natural gas, making this technology more environmentally damaging than current practices. This higher impact (calculated per kWh of electricity input to electrolysis) holds true even considering photovoltaic and wind electricity supply. These results are explained by the reduction of efficiency of the system in the methanation process and the impact associated with the CO_2 capture. These results seem to contradict results of other studies, which generally show an environmental benefit of CCU over conventional sources. However, most studies tend to focus on climate change only,

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

and results provided by Zhang et al.[103] demonstrate that considering additional environmental impact categories is essential.

Another issue that affects the methanation reaction is the heat management during the reaction. Shifting to new reactor designs and heat resistant catalysts with a higher sulfur tolerance would create more opportunities to overcome these challenges.[5,107]

In terms of commercial installations, Audi has an operational Power-to-Gas facility in Werlte (northern Germany) capable of producing 325 $Nm^3 h^{-1}$ of SNG from CO_2 methanation with renewable hydrogen generated from wind powered electrolysis.[108]

Similarly as with methanol, methane produced via CCU allows reducing GHG emissions only if water electrolysis powered by renewable energy is used to produce the hydrogen needed for the hydrogenation reaction. Nevertheless, the impacts of other environmental impact categories seem to be larger for CCU than for conventional production, even using renewable energy, particularly for human toxicity, freshwater ecotoxicity and resource depletion.

4.3. Dimethyl ether

DME is a product of the dehydration of methanol.[47] DME can be used as a diesel fuel due to its high cetane number (55–60) and clean burning properties, such as no soot, no SO_x emission and low NO_x emission. This allows the use of simpler exhaust systems in existing diesel vehicles. DME can also act like a liquefied petroleum gas (LPG) substitute in applications such as heating and cooking.[110] DME can be used to produce hydrocarbons, oxygenates and high ethers.[111] Specifically, there is a large market value for acetic acid, gasoline and olefins that can be derived from DME.

DME is an excellent solvent and also degrades rubber materials.[110] It has been increasingly used as an aerosol propellant to replace conventional chlorofluorocarbons that were found to destroy ozone layers of the atmosphere.[112] The DME aerosol propellant has been used in a wide range of personal care products, including shaving creams, hairspray, foams, and antiperspirants, because of its higher water solubility relative to other propellants. Besides, DME has been used in a limited amount to freeze meat and fish by direct immersion.[113,114]

DME can be synthesized either directly or by a two-step method from syngas. In the direct method, simultaneous methanol synthesis and in-site dehydration occur. In the indirect synthesis method, methanol is synthesized from syngas followed by methanol dehydration. From a cost and product-yield perspective, the direct synthesis of DME from syngas may be the preferred route for large scale industrial production.[115]

From a global warming point of view, DME utilizes a high amount of CO_2 for its synthesis (i.e., it locks in a large amount of CO_2): 1.91 $t_{CO_2}\ t^{-1}$.[74] Considering the production volume in 2011 of DME within the European Union, CO_2-based DME could avoid the emission of 100 $kt_{CO_2}\ y^{-1}$.[74]

Artz et al.,[64] based on data from Schakel et al.,[116] estimated that the global warming impact of CO_2-based DME was estimated to be equal to that of current fossil diesel in a projected 2020 scenario (0.09 $kg_{CO_2\ eq}\ MJ_{fuel}^{-1}$; Table 7). The impact of CO_2-based DME could be reduced further to 0.05 $t_{CO_2\ eq}\ MJ_{fuel}^{-1}$ by using wind energy instead of fossil energy. These numbers were calculated considering cradle-to-gate emissions from production, and combustion emissions computed assuming stoichiometry. In both current and wind-energy scenarios, the global warming impact is mainly caused by the DME combustion and direct emissions. The global warming impact reported in this study is significantly higher than cradle-to-grave emissions of conventionally-produced DME used as fuel estimated by Bongartz et al. ($\approx$0.02 $kg_{CO_2\ eq}\ MJ_{fuel}^{-1}$).[101]

In another study, Thonemann[29] concluded that CO_2-based DME production has lower environmental impact than conventional DME production for all impact categories within the ILCD 1.0.8 2018 midpoint method, except ecotoxicity and ozone depletion. In their modelling, they used 1 kg DME produced as functional unit, wind energy as source of electricity, attributional modelling, openLCA 1.9 software and the ecoinvent cut-off 3.5 database.

McKone et al.[110] compared the life-cycle carbon intensity of DME production from biogas from an anaerobic digestion process of food and yard waste (namely BioDME), with that of low-sulfur diesel and DME from natural gas. Although the carbon intensity of fuel production was higher for BioDME in this study, the authors found out that negative emissions were associated with feedstock production, making BioDME perform significantly better than the other two alternatives. This is because BioDME is considered to recycle carbon from the biogas produced by the anaerobic digestion. However, this is questionable, since the biogas produced by anaerobic digestion is supposed to be used for electricity and/or heating production, which would reduce the need to generate this electricity and/or heating. Omitting these avoided emissions is misleading, as otherwise the waste could have been disposed of by other methods, such as landfill.

The utilization of CO_2 from gunwood gasification for the production of bio-DME (different to the aforementioned BioDME) reduced up to 20% the environmental impact of the production process.[117] Bio-DME showed lower emissions than diesel (0.46 and 1.62 $t_{CO_2\ eq}\ km^{-1}$ respectively) and a lower impact on human health and ecosystem than diesel (55 and 68%, respectively).

In another example, Matzen and Demirel[96] applied the LCA methodology to study the environmental impacts of production of DME via methanol from CO_2 captured from a corn fermentation process used to produce ethanol, and hydrogen from water electrolysis powered by wind energy. Both the methanol and methanol-based DME studied outperform conventional fossil fuels (liquefied natural gas, ultra-low sulfur diesel and methanol or DME obtained from natural gas). The only case when conventional fossil fuel showed lower environmental impact is when comparing CO_2-based methanol with gasoline for volatile organic compound and CO emissions. Overall, CO_2-based methanol and DME reduce GHG emissions

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Table 7. CO_2 emissions of different methods to produce DME.

Technology/process	System boundaries	Hydrogen and electricity source	CO_2 emissions	Notes	Ref.
synthesis by dehydrogenation of methanol	cradle-to-gate		1.27 $kg_{CO_2\ eq}\ kg_{DME}^{-1}$	standard production (non-CCU)	[29]
DME from natural gas	cradle-to-grave, including feedstock production and transport, fuel production, distribution and reforming, and vehicle fueling and combustion		91.1 $g_{CO_2\ eq}\ MJ_{DME}^{-1}$	70% efficiency	[110]
CO_2 converted to syngas via dry reforming of methane (Ni/Rh/Al_2O_3 catalyst), then transformed into DME (γ-Al_2O_3 catalyst)		hydrogen production is excluded from the system boundaries	35.8 $g_{CO_2\ eq}\ MJ_{DME}^{-1}$	CO_2 capture is excluded from the system boundaries	[116]
CO_2 converted to syngas via dry reforming of methane (Ni/Rh/Al_2O_3 catalyst), then transformed into DME (γ-Al_2O_3 catalyst)	cradle-to-gate plus combustion	hydrogen production from steam methane reforming, electricity from EU-27 grid mix	0.15 $kg_{CO_2\ eq}\ MJ_{DME}^{-1}$	utilization of CO_2 captured from a coal power plant as feedstock is not included (-0.05 $kg_{CO_2\ eq}\ MJ_{DME}^{-1}$)	[64] (based on [116])
CO_2 converted to syngas via dry reforming of methane (Ni/Rh/Al_2O_3 catalyst), then transformed into DME (γ-Al_2O_3 catalyst)	cradle-to-gate plus combustion	hydrogen production from electrolysis with wind energy, electricity from EU-27 wind energy	0.12 $kg_{CO_2\ eq}\ MJ_{DME}^{-1}$	utilization of purified CO_2 as feedstock is not included (-0.06 $kg_{CO_2\ eq}\ MJ_{DME}^{-1}$	[64] (based on [116])
CO_2 converted to syngas via dry reforming of methane (Ni/Rh/Al_2O_3 catalyst), then transformed into DME (γ-Al_2O_3 catalyst)	cradle-to-gate	electricity from the German grid mix, hydrogen from polymer electrolyte membrane electrolysis	−0.48 $kg_{CO_2\ eq}\ kg_{DME}^{-1}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [92,116,120])
CO_2 converted to syngas via dry reforming of methane (Ni/Rh/Al_2O_3 catalyst), then transformed into DME (γ-Al_2O_3 catalyst)	cradle-to-gate	electricity from wind energy, hydrogen from polymer electrolyte membrane electrolysis	−1.07 $kg_{CO_2\ eq}\ kg_{DME}^{-1}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [92,116,120])
DME from high solid anaerobic digestion of food and yard waste	cradle-to-grave, including feedstock production and transport, fuel production, distribution and reforming, and vehicle fueling and combustion		−5 $g_{CO_2\ eq}\ MJ_{DME}^{-1}$		[110]
CO_2 converted to methanol, then transformed to DME via a condensation reaction	cradle-to-gate	hydrogen from electrolysis powered by wind energy	0.5 $t_{CO_2\ eq}\ MJ_{DME}^{-1}$	CO_2 captured from biomass fermentation	[96]
CO_2 enhanced gasification of gumwood to produce DME	cradle-to-gate including the pre-treatment process; production of DME; and utilization of DME as renewable fuel for diesel engines.	Chinese grid mix used for electricity	bio-DME emissions 46.2 $kg_{CO_2\ eq}$ per 100 km, and 162 $kg_{CO_2\ eq}$ per 100 km for diesel	functional unit was diesel and bio-DME fueled engine travelling a distance of 100 km by an urban bus; includes both direct and indirect emissions	[117]

by 82–86% and fossil fuel depletion by 82–91%. The authors also calculated the environmental impact results for several categories for both methanol and DME production. Unsurprisingly, methanol outperforms DME for all impact categories from cradle-to-gate, since DME is produced via the same route as methanol. When expanding the scope to cradle-to-grave (including emissions from the combustion), DME shows lower emissions of volatile organic compounds, CO, NO_x and SO_x, although higher GHG emissions and fossil fuel use.

KOGAS, a South Korean public natural gas company, has been manufacturing DME from CO_2 since 2000 on demonstration and pilot scale plants in Korea. In 2008, the demonstration plant production was 10 t day^{-1} of DME, and they target to produce 3000 t day^{-1} of DME.[85,118] Similarly, Oberon Fuels produce up to 10000 gallons of DME per day, from feedstocks like biogas from dairy manure and food waste, to service regional fuel markets in the US.[119] This DME is primarily used as a transportation fuel.

In conclusion, there seems to be consensus in that DME produced via CCU has the potential to reduce GHG emissions compared to conventional production methods. DME used as fuel does not increase life-cycle emissions compared to diesel.

4.4. Dimethyl carbonate

DMC represents a good substitute for some organic solvents or reagents (e.g., phosgene, dimethylsulfoxide, dimethyl sulfate or methyl iodide) that have an associated high environmental impact. DMC is also used as a methylating agent, as an additive

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

in petrol (as an octane improver)[5] and is applied as a replacement to ketones and acetates in paints and adhesives, due to its strong solvation power. Although traditionally DMC was produced via reacting phosgene and methanol, most production now is via oxidative carbonylation by reacting carbon monoxide, oxygen and methanol. Alternative routes include transesterification of ethylene carbonate or propylene carbonate and methanol.[121]

DMC needs 0.50 t_{CO_2} per t of DMC produced, which is only one fourth of the CO_2 used to produce DME.[74] Considering the production volume of DME in the European Union in 2011, CO_2-based DMC could avoid the emission of 300 kt_{CO_2} y^{-1}.[74] These authors conclude that DMC, along with methanol and DME, are well placed to be synthetized from CO_2 because of their potential to reduce CO_2 emissions and their economic feasibility.

There is a lack of LCA studies on the use of captured CO_2 to produce DMC. One of the few examples is an old article by Aresta and Galatola,[122] who compared a conventional route based on phosgene with an alternative utilizing CO_2 captured from an ammonia manufacturing plant, a steam reforming process and fossil fuel fired power plant. Production of CO_2-based DMC performs better than via phosgene for all environmental impact categories considered: greenhouse effect, ozone layer depletion, acidification, nutrification and oxidant formation. These results were consistent using either mass or economic allocation. For the CO_2-based process, the capture process contributes the most to the overall environmental impacts because of the high energy use to recover CO_2 with an MEA solution.

Despite some variability on the results reported by various sources, it seems that DMC production from CO_2 via ethylene carbonate and urea transesterification routes have a lower global warming impact than fossil-based DMC production,[64] with values between 0.45–0.77 $t_{CO_2\ eq}\ t_{DMC}^{-1}$ (gate-to-gate)[123,124] and 0.86 $t_{CO_2\ eq}\ t_{DMC}^{-1}$ (cradle-to-gate)[125] for the ethylene carbonate transesterification route, and between 0.34 $t_{CO_2\ eq}\ t_{DMC}^{-1}$ (cradle-to-gate)[125] and 2.93 $t_{CO_2\ eq}\ t_{DMC}^{-1}$ (gate-to-gate)[123] for the urea transesterification route (Table 8).

These results contrast with the results obtained by Thonemann,[29] who concluded that the environmental impact of producing DMC from CO_2 is higher than that of conventional production, for all impact categories considered with the ILCD 1.0.8 2018 midpoint method. This is mostly due to the high electrical and thermal energy, and water demand. In their modelling, they used "1 kg DMC produced" as functional unit, two scenarios with electricity from the German grid or wind electricity, attributional modelling, openLCA 1.9 software and the ecoinvent cut-off 3.5 database. This study is based on previous work by Garcia-Herrero et al.,[126] who analysed the electrochemical reaction of CO_2 and methanol in the presence of potassium methoxide and the ionic liquid 1-butyl-3-methylimidazolium bromide to produce DMC, and Kongpanna et al.[123] who analysed CO_2, urea, ethylene carbonate and propylene carbonate routes.

Specifically, Garcia-Herrero et al.[126] compared the environmental impact of a novel process to produce DMC via an electrochemical reaction of CO_2 with methanol with the environmental impact of the conventional process based on oxidative carbonylation of methanol. The novel method had a much higher environmental impact than the conventional one for a range of environmental impact categories considered (between 11 and 111 times higher) due to the very low conversion achieved and large energy use in the separation process. The authors found that the conversion in the novel process should increase from 0.7 to 20% to perform environmentally better than the conventional process.

Using CO_2 captured with MEA to produce DMC in the urea-based process reduces the global warming potential by 4.3 times compared to the conventional synthesis of DMC from phosgene (31 vs. 132 $t_{CO_2\ eq}\ t_{DMC}^{-1}$).[5,122] The authors used a cradle-to-gate approach, excluding recycling and disposal stages. The boundaries included CO_2 separation and capture, its compression, transport and chemical synthesis. The reductions in the other environmental impacts were similar, ranging from 3.6 times for the eutrophication potential, four times for the acidification potential and photochemical ozone creation potential, to 13 times for the ozone depletion potential. The main reason for this difference is the reduced energy requirements for the production of raw materials used in the urea-based synthesis (hydrogen, ammonia and CO_2 recovered with MEA), compared to the production of raw materials used in the phosgene-based process (chlorine and sodium hydroxide).

In conclusion, there is no clear agreement among the studies on the environmental advantages of CCU-based DMC over conventionally produced DMC. Some studies report a reduction of environmental impacts, but other studies claim that the environmental impact of such CCU methods is significantly higher than existing technologies. This holds true for most environmental impact categories. Based on this, further analysis of the life-cycle environmental impacts of different methods to produce DMC via consistent LCA is needed.

4.5. Propane, propene, and other light hydrocarbons

Currently, olefins are mostly produced by thermal steam cracking of naphtha, which is an energy intensive process. This generates large CO_2 emissions of 1.2–3 t_{CO_2} per t of olefin obtained.[127,128] Methanol to olefins is a widely studied alternative that has started to be applied at large scale. The first commercial methanol-to-olefins plant was launched in 2010 in China, with a production rate of 600 $kt\,y^{-1}$.[129]

Paraffins and olefins can be synthetized from CO_2 by indirect routes (via methanol or carbon monoxide) or by direct routes, such as CO_2-based Fischer-Tropsch synthesis or with bifunctional catalysts. Direct routes tend to perform better environmentally.[130]

Olefins production (e.g., propene) from fossil sources or CO_2 has associated a high energy use, and therefore would benefit more significantly if this energy comes from renewable sources.[131] It has been estimated that utilizing hydrogen from low-carbon electricity sources (e.g., electrolysis powered by

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Table 8. CO_2 emissions of different methods to produce DMC.

Technology/process	System boundaries	Hydrogen and electricity source	CO_2 emissions	Notes	Ref.
conventional production	cradle-to-gate		2.12 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	standard production (non-CCU)	[29]
via phosgene from CO and Cl_2	cradle-to-gate	European electricity mix (from 1998)	132 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	standard production (non-CCU), mass allocation	[122]
partial carbonylation (Bayer process)	cradle-to-gate		0.52 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	standard production (non-CCU)	[123]
direct synthesis from CO_2 and methanol	cradle-to-gate	electricity from the German grid mix, hydrogen from polymer electrolyte membrane electrolysis	7.33 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [123])
electrochemical reaction of CO_2 with methanol in the presence of potassium methoxide and 1-butyl-3-methylimidazolium bromide	cradle-to-gate	electricity from the German grid mix, hydrogen from polymer electrolyte membrane electrolysis	465 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [126])
direct synthesis from CO_2 and methanol	cradle-to-gate	electricity from wind energy, hydrogen from polymer electrolyte membrane electrolysis	7.26 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [123])
electrochemical reaction of CO_2 with methanol in the presence of potassium methoxide and 1-butyl-3-methylimidazolium bromide	cradle-to-gate	electricity from wind energy, hydrogen from polymer electrolyte membrane electrolysis	381 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	no environmental impact allocated to the generation of CO_2 used as feedstock	[29] (based on [126])
via urea from NH_3 and CO_2	cradle-to-gate	European electricity mix (from 1998), hydrogen from steam reforming	30.6 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	mass allocation	[122]
via ethylene oxide	cradle-to-gate		0.86 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$		[64] (based on [125])
via urea methanolysis	cradle-to-gate		0.34 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$		[64] (based on [125])
transesterification of ethylene carbonate	cradle-to-gate		0.45 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$		[123]
transesterification of urea	cradle-to-gate		2.94 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$		[123]
transesterification of ethylene carbonate	cradle-to-gate	electricity emissions of 35.902 $kg_{CO_2\ eq}$ MMBtu (million British thermal unit)$^{-1}$	0.77 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	does not include the utilization of −0.70 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$ as feedstock	[124]
oxidative carbonylation of methanol (Eni)	cradle-to-gate	electricity from the Spanish grid and solar photovoltaics	3.18 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$		[126]
electrosynthesis from CO_2 and methanol	cradle-to-gate	electricity from the Spanish grid and solar photovoltaics	78.9 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$	includes the utilization of −0.49 $kg_{CO_2\ eq}\ kg_{DMC}^{-1}$ as feedstock	[126]

renewable energy) and captured CO_2 to produce propene has the potential to avoid 1.89 t CO_2 emissions per t of propene produced.[43] On the other hand, CO_2-based C_{3+} chemicals have a higher potential to reduce greenhouse gases in the atmosphere compared to smaller molecules, since they need more CO_2 per molecule of product obtained.

Mota and Kim[128] claimed that, out of the several methods to produce chemicals from CO_2, photochemical synthesis seems to be the most energy efficient, followed by electrochemical synthesis, with thermochemical synthesis being the least energy efficient. On the other hand, thermochemical synthesis shows the highest selectivity for olefins, whilst photochemical synthesis has the lowest selectivity.

Jiang et al.[129] assessed the gasification of biomass and use of CO_2 to produce olefins by two methods to generate syngas: using steam and oxygen for the gasification process in a reactor combined with a catalytic reforming unit (direct method) and using steam in a gasifier connected with a combustor (indirect method). They found that for both processes the biomass production and direct emissions (i.e., combustion) account for the largest contribution for CO_2 emissions per t of olefins produced, and although CO_2 emissions from biomass production were similar in both cases, CO_2 emissions from combustion were nearly four times larger for the indirect process. Nevertheless, the significant negative emissions for both methods make the net CO_2 emissions negative (−4.44 $t_{CO_2\ eq}\ t_{olefins}^{-1}$ for the indirect method and −8.74 $t_{CO_2\ eq}\ t_{olefins}^{-1}$ for the direct method).

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

The better sustainability performance of the direct method is explained by the large emissions of the char combustion to provide the heat for the biomass gasifier of the indirect method, whereas the CO_2 emitted in the gasification, tar reforming and water gas shift reaction, was captured in the direct method.

There are several studies that analyzed the production of Fischer–Tropsch fuels from CO_2. For instance, Cuéllar-Franca et al.[132] studied the life-cycle environmental impacts and costs of four different processes to produce Fischer-Tropsch fuels from the CO_2 captured from anaerobic digestion of sewage sludge. They found out that the environmental performance of the CO_2-based systems significantly improves when scaling up due to economies of scale. At large scale, these CO_2-based fuels perform better than fossil diesel for the following environmental impact categories studied: abiotic depletion of elements and fossil resources potentials, acidification potential, eutrophication potential, human toxicity potential, photochemical oxidants creation potential, freshwater aquatic ecotoxicity potential, marine aquatic ecotoxicity potential and terrestrial ecotoxicity potential. This is one of the few studies that considers a wide range of environmental impact categories in its analysis of CCU technologies. Fossil diesel performs better only for global warming potential and ozone layer depletion potential. However, optimising key parameters of the CO_2-based systems, global warming potential can be reduced to become even 70% lower than for diesel.

One of the first LCA studies of CCU technologies was undertaken by van der Giesen et al.[133] They compared the reduction on CO_2 emissions of various Fischer–Tropsch processes to produce fuels from CO_2 via carbon monoxide and using hydrogen from water electrolysis. They concluded that, comparing with fossil-based fuels, CO_2-based fuels only provide a reduction on CO_2 emissions when solar energy is used, and the CO_2 is captured from atmosphere. In all other cases, conventional production of fuels from fossil resources is superior from a CO_2 emissions angle. Although they were skeptical about the global carbon mitigation that CCU can provide, they noted that novel technologies, as those that have been investigated and developed since the article was published, would improve the performance of CCU. Particularly, they highlighted the potential of CCU to provide fuels for airplanes and heavy-goods vehicles.

Hombach et al.[134] studied the production of Fischer–Tropsch fuels from CO_2 captured from air, using wind energy and different water electrolysis systems. Life-cycle GHG emissions could be as low as 64 $g_{CO_2\,eq}\ MJ_{fuel}^{-1}$ in a 2015 scenario (in Germany), but this could be further reduced to 6.6 $g_{CO_2\,eq}\ MJ_{fuel}^{-1}$ in a 2030 scenario. Both results are lower than for conventional production via fossil fuel (84 $g_{CO_2\,eq}\ MJ^{-1}$). These results significantly change if the German grid mix is used as the source of electricity instead of wind energy, with values of 441 $g_{CO_2\,eq}\ MJ^{-1}$ in a 2015 scenario and 148 $g_{CO_2\,eq}\ MJ^{-1}$, respectively, in a 2030 scenario. In both cases, they are larger values than current production via fossil fuels.

With regard to the catalysts needed for the reactions, composite zeolite-based catalysts have been successfully used to convert CO_2 into gasoline-range hydrocarbons.[135] Nevertheless, large-scale production of zeolites needs large amounts of energy, high pressures and long reaction times, and consequently, current research is looking into producing zeolites greenly and more efficiently, for instance by organic-template-free, ionothermal, solvent-free and microwave synthesis.[135]

Another CCU option is to gasify municipal solid waste and use the syngas to produce valuable chemicals. This is in line with the waste biorefinery concept, commonly used in recent years in the agri-food sector.[136] This option, which allows producing chemicals such as olefins, DME and methanol, can be considered environmentally sustainable and is generally preferred over other treatments (e.g., incineration) to deal with solid waste.[136] Similar approaches were recommended by Jiang et al.,[129] who used biomass as the starting raw material, and Peters et al.,[137] who proposed using manure and municipal solid waste as feedstock for CO_2 in Power-to-Gas projects. The use of liquid manure for this purpose would result in not only a reduction of CO_2 emissions (the authors report a net value of $-85.6\ g_{CO_2}$ per MJ of generated fuel), but also reducing acidification and eutrophication of soil and water by avoiding land spreading this material.

In conclusion, there are a wide range of other chemicals that can be produced from CO_2, such as light hydrocarbons. Examples of this include propane (a paraffin) and propene or propylene (an olefin). For these products, LCAs that quantify their environmental impact are lacking. With the published data available, production of light hydrocarbons from CO_2 may reduce environmental impacts, particularly GHG emissions, if renewable energy and hydrogen from water electrolysis is used.

5. Use of LCA to Analyze Environmental Impacts of CCU Technologies

Several researchers[19–23] have recommended LCA as an appropriate methodology to evaluate environmental impacts of CCU technologies. Although historically few LCA studies of CCU systems had been undertaken,[5,24–27] the number of these studies started recently to grow, as shown in this article. Examples of such approaches are an LCA study of a Power-to-Gas plant in Switzerland undertaken by the Paul Scherrer Institute and an LCA analysis of hydrogen production via fermentation and its conversion to methane by the Energy Institute of the Johannes Kepler University Linz.[138]

Several methodological choices in LCA studies can significantly influence results. For instance, the reduction in GWP is sensitive to CO_2 capture and allocation methods as well as the assumptions for heat recovery from the system.[5] Furthermore, a number of studies focus on climate change or global warming only, omitting the rest of the environmental impact categories. In order to understand the full life-cycle picture of the process and products studied, as many as possible environmental impact categories must be used.[27,84,103,132]

The timing of the capture of CO_2 and subsequent emissions should also be accounted,[139] and this is often lacking.

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

Chemicals or fuels produced from CO_2 offer temporary storage of CO_2 (very short in the case of fuels). LCA do not account for emissions timing.[28,140] Several methods have been proposed for this purpose.[28] In the absence of an accepted method, standards currently recommend to separately report the amount stored and the duration of the temporary storage.[113,114]

In order to solve any allocation issues, ISO recommends using the multi-functionality hierarchy with system expansion, substitution or allocation. Zhang et al.[103] undertook an LCA of Power-to-Gas (for hydrogen and methane production) and claimed that system expansion provides more meaningful results than subdivision (based on causalities). In fact, in their study, the GHG emissions associated with synthetic natural gas production from Power-to-Methane using the subdivision approach are higher than those of conventional natural gas, in contrast with results obtained using system expansion including electricity production (if a power plant is considered) or cement production (if a cement plant is considered). Other researchers[106,141,142] also recommend system expansion to deal with multifunctionality. However, when comparing CO_2-based products to other products, allocation might be necessary in some cases.[106] In order to ease data collection and calculations, Abanades et al.[24] recommends applying comparative analysis of systems with and without CCU and therefore obviate elements present in both systems.

Koj et al.[84] highlighted the lack of transparency on the life-cycle inventory and several methodological choices of LCA studies of Power-to-X. They found that the most common functional unit used was based on energy and the system boundary usually covered the factory gate. About half of the studies analysed by Koj et al.[84] did not specify how multi-functionality issues were approached. A variety of life-cycle impact assessment methods was used (e.g., CML, ILCD, ReCiPe). Endpoint indicators, in addition to midpoint indicators, were rarely used. All studies used attributional LCA, which indicates the need to also consider consequential approaches for LCA. Most practitioners used the ecoinvent database, followed by GaBi. Most studies analysed Power-to-X under current conditions and only in Europe. The same conclusions were obtained by Thonemann[29] in their review of CCU studies in the chemical sector. Artz et al.[64] also found significantly different results for LCA studies carried out for the same CO_2-based product manufactured by the same route, which proves that a common framework for LCA of CCU is needed. They identified the reasons for such variations as different assumptions about the supply of feedstocks (e.g., CO_2, H_2 and electricity), definition of the system boundaries, and the way to allocate products and co-products. Thonemann[29] identified the selection of system boundaries, functional unit and allocation method, as the most relevant methodological choices in environmental impact studies of CCU. They found that cradle-to-gate systems, output-based functional units based on mass (e.g., "producing 1 kg of methanol") and system expansion are more commonly considered. In terms of technological choices, most studies considered CO_2 captured from combustion, hydrogen from water splitting, and the national grid mix as source of electricity.[29] Construction and transport are often excluded in these analysis.

Von der Assen et al.[143] published a thorough analysis of potential pitfalls in LCA for CCU, which they identified as: 1) intuitively characterizing utilized CO_2 as a negative GHG emission, 2) allocation of environmental impacts to individual products in multifunctional processes, and 3) overestimating the effect of the CO_2 storage duration on the global warming impact. In the same study, they presented a framework to avoid such pitfalls of LCA for CCU. Zhang et al.[103] also highlighted the lack of consensus on the methodological issues for environmental assessment of CCU and underlined that von der Assen's framework has not been consistently applied as of yet for Power-to-Gas systems. von der Assen et al.[28] also provided a useful introductory-level tutorial of LCA for CCU, which can also be found in a summarized form in Ref..[15]

In agreement with the several aspects discussed in this section, CarbonNext[144] gave the following recommendations to apply LCA to study CCU systems:

- When CO_2-based products are compared with the same product manufactured conventionally, combustion, use and end-of-life are identical in both scenarios, and a cradle-to-gate analysis is recommended.
- The study should be location specific if possible.
- System expansion should be used to address multifunctional processes and the functional unit should be extended accordingly to account for these additional products.
- CO_2 capture should be included in the study if possible.

In order to further support the application of LCA to study CCU systems, Zimmermann et al.[142] recently published a set of useful and detailed guidelines. These guidelines describe the four LCA phases (from ISO 14040) and explain how they should be approached in CCU studies. They distinguished between mandatory and optional actions ("shall", "should", "may") for each of the LCA phases and include a "checklist" to help the practitioner to complete all actions required in the LCA. They also published several worked examples to illustrate how the guidelines should be applied.[145]

According to these guidelines,[142] the following functional units may be used in CCU studies: energy content, unit of energy service, mass, unit of technical performance, or satisfaction of the energy demand. The selection of the functional unit depends on the CCU purpose (i.e., energy storage, a chemical or a fuel) and the alternative CCU product to which the CCU product is compared to. They only recommend using a cradle-to-gate approach when the two products compared are the same and using a cradle-to-grave approach for different products and for energy storage.

Zimmermann et al.[142] recommends using the CML method for the Life-Cycle Impact Assessment phase, and a second method depending on the geographical scope (e.g., ILCD for Europe and TRACI for US). Also, they recommend using only midpoint indicators in the assessment, due to the high uncertainty of endpoint indicators and single scores. On the other hand, endpoint indicators and single scores are particularly useful when comparing products or processes, as CCU studies do. Therefore, the following ISO recommendations would be the most appropriate approach: showing results with midpoint indicators (mandatory) and utilizing endpoint indica-

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

tors and, particularly, single scores (optionally) only when comparative assertions are not to be disclosed to the public.[141]

Our conclusions from the LCAs reviewed of CCU technologies is that a number of methodological choices significantly influence LCA results. The selection of the functional unit is a key step, and this should differ depending on the CCU product produced. The system boundaries should include all relevant processes (e.g., carbon capture), only excluding those that are common for two scenarios in comparative analyses. In multifunctional processes, system expansion must be prioritized. A geographical scope must be defined, as this significantly influences several methodological choices (e.g., electricity source). The timing of the emissions should be considered, as this is very different. for example, for fuels (very short) or construction materials (very long). All assumptions and simplifications should be justified and sufficiently described. The quality of data should be assessed. CCU decisions should not be undertaken based only on GHG emissions, but a wide range of environmental impact categories should be considered. An updated and reliable life-cycle impact assessment method must be used, such as CML, ILCD or ReCiPe. Uncertainty and sensitivity analyses must be performed to assess the quality and robustness of the results obtained. Finally, all aspects described above should be documented in the LCA report.

6. Summary and Outlook

This Review has shown that carbon capture and utilization (CCU) can be an alternative to manufacture valuable chemicals, such as methanol, methane, dimethyl ether (DME) and dimethyl carbonate (DMC), whilst reducing environmental impacts when compared to standard practices. In the chemical industry, CCU could reduce CO_2 emissions, while at the same time decrease the dependence on fossil fuels as carbon source for chemical production.

Nevertheless, using CO_2 as feedstock does not guarantee sustainable or environmental production processes per se. Life Cycle Assessment (LCA) of prospective products could help to assess environmental impacts of the production processes, identify hotspots, guide future research and provide performance targets. The number of LCA studies on CCU has been growing over the last five years. However, there are still some CCU products, such as propane and propene, that have not been analyzed from a full LCA perspective. Also, different LCA studies of the same or similar CCU processes often give divergent results, which highlights the need to harmonize the LCA methodology in CCU studies.

LCA should not only be limited to impacts on climate change. Instead, a wide range of environmental impacts should be considered to avoid burden shifting to other impact categories, for instance reducing climate change impact at the expense of increasing toxicity. These tradeoffs need to be systematically analyzed. Sensitivity analysis should also be used to assess the assumptions made, such as efficiencies, allocation methods, estimated data and the actual lifetime storage of CO_2 in products.

Uncertainty in the data and results are common, particularly for low Technology Readiness Level (TRL) technologies. Such is the case for many CCU processes. The quality of the data collected therefore, must be reported. On the other hand, early technology assessments provide the greatest opportunity to influence design and environmental performance. Considering both the level of technology maturity and the level of maturity of the market into which the technology will be deployed, are critical defining factors of the emerging technology assessments.

Finally, it is important to note that LCA only provides environmental information of the prospective CCU technologies, but other considerations are equally important, such as socio-economic factors. It is recommended to integrate LCA studies with economic analysis, such as life-cycle costing (LCC) or techno-economic assessments (TEA) (which also considers technical factors). Integrating insights from public acceptance and social impact assessments (e.g., social LCA) into the research and development process could also become key for the future implementation of CCU.

In conclusion, CCU research is increasing and new products from CO_2 are continuously emerging onto the market. For example, you can now buy mattresses produced with CO_2 incorporated into the polymer chain, drink vodka produced from CO_2 captured from the air, use building materials such as aggregates made from CO_2 combined with other wastes or fill your car with fuel containing CO_2-derived methanol. CO_2 utilization seems set to make a contribution towards moving to a more circular, sustainable economy with lower environmental impacts.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: carbon capture and utilization · environmental analysis · life-cycle analysis · sustainable chemistry · renewable resources

[1] M. Crippa, G. Oreggioni, G. D, M. Muntean, E. Schaaf, E. Lo Vullo, E. Solazzo, F. Monforti-Ferrario, J. G. Olivier, E. Vignati, *Fossil CO_2 and GHG Emissions of All World Countries – 2019 Report, EUR 29849 EN*, **2019**.
[2] IPCC, Global Warming of 1.5 °C. An IPCC Special Report on the Impacts of Global Warming of 1.5 °C above Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change, **2018**.
[3] United Nations – Framework Convention on Climate Change, *Adoption of the Paris Agreement. FCCC/CP/2015/L.9/Rev.1*, **2015**.

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

[4] Scientific Advice Mechanism (SAM). Group of Chief Scientific Advisors. Scientific Opinion 4/2018, *Novel Carbon Capture and Utilisation Technologies*, **2018**.
[5] R. M. Cuéllar-Franca, A. Azapagic, *J. CO_2 Util.* **2015**, *9*, 82–102.
[6] N. Mac Dowell, P. S. Fennell, N. Shah, G. C. Maitland, *Nat. Clim. Change* **2017**, *7*, 243–249.
[7] International Energy Agency, Putting CO_2 to Use: Creating Value from Emissions, OECD, **2019**.
[8] T. Bruhn, H. Naims, B. Olfe-Kräutlein, *Environ. Sci. Policy* **2016**, *60*, 38–43.
[9] T. Niass, J. Kislear, Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage. Report of the Carbon Capture, Utilization and Storage Experts' Workshop, **2017**.
[10] European Commission, Pathways to Sustainable Industries. Energy Efficiency and CO2 Utilisation, **2018**.
[11] Zero Emissions Platform, Role of CCUS in a below 2 Degrees Scenario, **2018**.
[12] H. Naims, *Environ. Sci. Pollut. Res.*. **2016**, *23*, 22226–22241.
[13] C. Hepburn, E. Adlen, J. Beddington, E. A. Carter, S. Fuss, N. Mac Dowell, J. C. Minx, P. Smith, C. K. Williams, *Nature* **2019**, *575*, 87–97.
[14] R. J. Detz, B. van der Zwaan, *Energy Policy* **2019**, *133*, 110938.
[15] N. von der Assen, A. M. L. Lafuente, M. Peters, A. Bardow in *Carbon Dioxide Utilisation: Closing Carbon Cycle* (Eds.: P. Styring, E. A. Quadrelli, K. Armstrong), Elsevier, **2015**.
[16] G. Garcia-Garcia, S. Rahimifard, *Resour. Conserv. Recycl.* **2019**, *149*, 1–11.
[17] ISO, "ISO 14040:2006. Environmental management - Life cycle assessment - Principles and framework," can be found under https://www.iso.org/standard/37456.html, **2006**.
[18] ISO, "ISO 14044:2006. Preview Environmental management - Life cycle assessment - Requirements and guidelines," can be found under https://www.iso.org/standard/38498.html, **2006**.
[19] S. Han, S. Kim, Y. T. Kim, G. Kwak, J. Kim, *Energy Convers. Manage.* **2019**, *187*, 1–14.
[20] J. Albo, M. Alvarez-Guerra, P. Castaño, A. Irabien, *Green Chem.* **2015**, *17*, 2304–2324.
[21] I. Dimitriou, P. García-Gutiérrez, R. H. Elder, R. M. Cuéllar-Franca, A. Azapagic, R. W. K. Allen, *Energy Environ. Sci.* **2015**, *8*, 1775–1789.
[22] G. A. Ozin, *Adv. Mater.* **2015**, *27*, 1957–1963.
[23] E. A. Quadrelli, K. Armstrong, P. Styring in *Carbon Dioxide Utilisation: Closing Carbon Cycle* (Eds.: P. Styring, E. A. Quadrelli, K. Armstrong), Elsevier, **2015**, pp. 285–302.
[24] J. C. Abanades, E. S. Rubin, M. Mazzotti, H. J. Herzog, *Energy Environ. Sci.* **2017**, *10*, 2491–2499.
[25] R. S. Norhasyima, T. M. I. Mahlia, *J. CO_2 Util.* **2018**, *26*, 323–335.
[26] University of Michigan, Global Roadmap for Implementing CO2 Utilization, **2016**.
[27] D. Parra, X. Zhang, C. Bauer, M. K. Patel, *Appl. Energy* **2017**, *193*, 440–454.
[28] N. von Der Assen, P. Voll, M. Peters, A. Bardow, *Chem. Soc. Rev.* **2014**, *43*, 7982–7994.
[29] M. A. N. Thonemann, *Appl. Energy* **2020**, *263*, 114599.
[30] J. Stone, S. Rahimifard, *Supply Chain Manage.* **2018**, *23*, 207–238.
[31] D. Denyer, D. Tranfield in *Sage Handbook of Organic Research Methods* (Eds.: D. A. Buchanan, A. Bryman), Sage Publications Ltd., Thousand Oaks, California, USA, **2009**, pp. 671–689.
[32] N. von der Aßen, From Life-Cycle Assessment towards Life-Cycle Design of Carbon Dioxide Capture and Utilization, RWTH Aachen University, **2015**.
[33] C. Bosch, W. Meiser, *Process of Manufacturing Urea*, **1922**, 1,429,483.
[34] R. Chauvy, N. Meunier, D. Thomas, G. De Weireld, *Appl. Energy* **2019**, *236*, 662–680.
[35] C. Ampelli, S. Perathoner, G. Centi, *Philos. Trans. R. Soc. London Ser. A* **2015**, *373*, 20140177.
[36] E. A. Quadrelli, G. Centi, J.-L. Duplan, S. Perathoner, *ChemSusChem* **2011**, *4*, 1194–1215.
[37] EARTO, **2014**.
[38] C. Temvuttirojn, N. Chuasomboon, T. Numpilai, K. Faungnawakij, M. Chareonpanich, J. Limtrakul, T. Witoon, *Fuel* **2019**, *241*, 695–703.
[39] S. Michailos, S. McCord, V. Sick, G. Stokes, P. Styring, *Energy Convers. Manage.* **2019**, *184*, 262–276.
[40] Grand View Research, Propane Market Analysis, By End-Use (Industrial, Commercial, Residential, Transportation, Agriculture, Chemicals and Refineries), Value Chain Analysis, Industry Dynamics And Segment Forecasts, 2018–2025, **2017**.
[41] S. Li, L. Guo, T. Ishihara, *Catal. Today* **2020**, *339*, 352–361.
[42] B.-Y. Yu, I.-L. Chien, *Chem. Eng. Technol.* **2016**, *39*, 2304–2311.
[43] A. M. Bazzanella, F. Ausfelder, *DECHEMA, Eur. Chem. Ind. Counc.* **2017**, *168*.
[44] CarbonNext, Deliverable 2.3: Selection of Most Relevant Processes for Further Investigation, **2018**.
[45] J. Ott, V. Gronemann, F. Pontzen, E. Fiedler, G. Grossmann, D. B. Kersebohm, G. Weiss, C. Witte in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag, Weinheim, Germany, **2012**.
[46] F. D. Meylan, V. Moreau, S. Erkman, *J. CO_2 Util.* **2015**, *12*, 101–108.
[47] K. Takeishi, *Biofuels* **2010**, *1*, 217–226.
[48] A. ElMekawy, H. M. Hegab, G. Mohanakrishna, A. F. Elbaz, M. Bulut, D. Pant, *Bioresour. Technol.* **2016**, *215*, 357–370.
[49] DOE Energy Information Administration National Energy Information Center, *Propane Prices. What Consumers Should Know*, **2006**.
[50] Independent Commodity Intelligence Services, "Propylene Production and Manufacturing Process | ICIS," can be found under https://www.icis.com/explore/resources/news/2007/11/06/9076456/propylene-production-and-manufacturing-process/, **2019**.
[51] G. Reiter, J. Lindorfer, *J. CO_2 Util.* **2015**, *10*, 40–49.
[52] K. Damen, M. Van Troost, A. Faaij, W. Turkenburg, *Prog. Energy Combust. Sci.* **2006**, *32*, 215–246.
[53] E. S. Rubin, H. Mantripragada, A. Marks, P. Versteeg, J. Kitchin, *Prog. Energy Combust. Sci.* **2012**, *38*, 630–671.
[54] T. Kuramochi, A. Ramírez, W. Turkenburg, A. Faaij, *Prog. Energy Combust. Sci.* **2012**, *38*, 87–112.
[55] Z. Z. Yang, L. N. He, J. Gao, A. H. Liu, B. Yu, *Energy Environ. Sci.* **2012**, *5*, 6602–6639.
[56] A. Kätelhön, R. Meys, S. Deutz, S. Suh, A. Bardow, *Proc. Natl. Acad. Sci. USA* **2019**, *166*, 11187–11194.
[57] K. Armstrong, Youssef Travaly, H. Bolscher, T. Brun, H. Knippels, D. Kraemer, N. Rothengatter, G. Wilson, P. Styring, E. Veenstra, G. Saussez, L. Buck, *A Strategic European Research and Innovation Agenda for Smart CO_2 Transformation in Europe*, **2016**.
[58] X.-L. Du, Z. Jiang, D. S. Su, J.-Q. Wang, *ChemSusChem* **2016**, *9*, 322–332.
[59] G. A. Olah, *Angew. Chem. Int. Ed.* **2005**, *44*, 2636–2639; *Angew. Chem.* **2005**, *117*, 2692–2696.
[60] S. Brynolf, E. Fridell, K. Andersson, *J. Cleaner Prod.* **2014**, *74*, 86–95.
[61] K. Atsonios, M. A. Kougioumtzis, K. D. Panopoulos, E. Kakaras, *Appl. Energy* **2015**, *138*, 346–366.
[62] S Eggleston, L Buendia, K Miwa, T Ngara, K Tanabe, "IPCC Guidelines for National Greenhouse Gas Inventories," can be found under https://www.ipcc-nggip.iges.or.jp/public/2006gl/, **2006**.
[63] M. Pérez-Fortes, J. C. Schöneberger, A. Boulamanti, E. Tzimas, *Appl. Energy* **2016**, *161*, 718–732.
[64] J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* **2018**, *118*, 434–504.
[65] S. Alsayegh, J. R. Johnson, B. Ohs, M. Wessling, *J. Cleaner Prod.* **2019**, *208*, 1446–1458.
[66] H. Firmansyah, Y. Tan, J. Yan in *Energy Procedia*, Elsevier Ltd., **2018**, pp. 576–581.
[67] S. Fukuzumi, *Joule* **2017**, *1*, 689–738.
[68] T. Liu, Q. Liu, J. Lei, J. Sui, H. Jin, *Appl. Energy* **2018**, *225*, 380–391.
[69] C. F. Shih, T. Zhang, J. Li, C. Bai, *Joule* **2018**, *2*, 1925–1949.
[70] F. Trieb, M. Moser, J. Kern, *Energy* **2018**, *153*, 1–11.
[71] L. Wang, M. Ghoussoub, H. Wang, Y. Shao, W. Sun, A. A. Tountas, T. E. Wood, H. Li, J. Y. Y. Loh, Y. Dong, M. Xia, Y. Li, S. Wang, J. Jia, C. Qiu, C. Qian, N. P. Kherani, L. He, X. Zhang, G. A. Ozin, *Joule* **2018**, *2*, 1369–1381.
[72] G. A. Olah, A. Goeppert, G. K. S. Prakas, *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, **2009**.
[73] M. Khanipour, A. Mirvakili, A. Bakhtyari, M. Farniaei, M. R. Rahimpour, *Int. J. Hydrogen Energy* **2019**, *45*, 7386–7400.
[74] A. Otto, T. Grube, S. Schiebahn, D. Stolten, *Energy Environ. Sci.* **2015**, *8*, 3283–3297.
[75] T. B. H. Nguyen, E. Zondervan, *J. CO_2 Util.* **2019**, *34*, 1–11.
[76] D. Milani, R. Khalilpour, G. Zahedi, A. Abbas, *J. CO_2 Util.* **2015**, *10*, 12–22.
[77] M. Rumayor, A. Dominguez-Ramos, A. Irabien, *J. Cleaner Prod.* **2019**, *225*, 426–434.
[78] N. Meunier, R. Chauvy, S. Mouhoubi, D. Thomas, G. De Weireld, *Renewable Energy* **2020**, *146*, 1192–1203.
[79] J. Kim, C. A. Henao, T. A. Johnson, D. E. Dedrick, J. E. Miller, E. B. Stechel, C. T. Maravelias, *Energy Environ. Sci.* **2011**, *4*, 3122–3132.

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH

[80] J. Kim, T. A. Johnson, J. E. Miller, E. B. Stechel, C. T. Maravelias, *Energy Environ. Sci.* **2012**, *5*, 8417–8429.
[81] J. Kim, J. E. Miller, C. T. Maravelias, E. B. Stechel, *Appl. Energy* **2013**, *111*, 1089–1098.
[82] I. Ganesh, *Renewable Sustainable Energy Rev.* **2014**, *31*, 221–257.
[83] A. G. Chaplin, Renewable Methanol: An Analysis of Technological Potentials in Light of the EU Biofuels Policy Objectives of Greenhouse Gas Savings, Security of Supply and Employment, Aalborg University, **2013**.
[84] J. C. Koj, C. Wulf, P. Zapp, *Renewable Sustainable Energy Rev.* **2019**, *112*, 865–879.
[85] F. Pontzen, W. Liebner, V. Gronemann, M. Rothaemel, B. Ahlers, *Catal. Today* **2011**, *171*, 242–250.
[86] I. Ganesh, *Renewable Sustainable Energy Rev.* **2016**, *59*, 1269–1297.
[87] J. Harnisch, C. Jubb, A. Nakhutin, V. C. S. Cianci, R. Lanz, T. Martinsen, A. K. W. Mohammad, M. M. O. Santos, B. T. Mader, A. McCulloch in *IPCC Guidelines for National Greenhouse Gas Inventories*, **2006**.
[88] F. Safari, I. Dincer, *Energy Convers. Manage.* **2018**, *177*, 693–703.
[89] W. Hoppe, N. Thonemann, S. Bringezu, *J. Ind. Ecol.* **2018**, *22*, 327–340.
[90] V. Uusitalo, S. Väisänen, E. Inkeri, R. Soukka, *Energy Convers. Manage.* **2017**, *134*, 125–134.
[91] A. Sternberg, C. M. Jens, A. Bardow, *Green Chem.* **2017**, *19*, 2244–2259.
[92] C. Fernández-Dacosta, L. Shen, W. Schakel, A. Ramirez, G. J. Kramer, *Appl. Energy* **2019**, *236*, 590–606.
[93] P. Biernacki, T. Röther, W. Paul, P. Werner, S. Steinigeweg, *J. Cleaner Prod.* **2018**, *191*, 87–98.
[94] M. Aresta, A. Caroppo, A. Dibenedetto, M. Narracci in Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century, Springer US, **2002**, pp. 331–347.
[95] A. Sternberg, A. Bardow, *Energy Environ. Sci.* **2015**, *8*, 389–400.
[96] M. Matzen, Y. Demirel, *J. Cleaner Prod.* **2016**, *139*, 1068–1077.
[97] W. Zhao, B. Zhang, G. Wang, H. Guo, *J. Energy Chem.* **2014**, *23*, 201–206.
[98] ENEA Consulting, "The Potential of Power-To-Gas," **2016**.
[99] S. K. Hoekman, A. Broch, C. Robbins, R. Purcell, *Int. J. Greenhouse Gas Control* **2010**, *4*, 44–50.
[100] M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, *Renewable Energy* **2016**, *85*, 1371–1390.
[101] D. Bongartz, L. Doré, K. Eichler, T. Grube, B. Heuser, L. E. Hombach, M. Robinius, S. Pischinger, D. Stolten, G. Walther, A. Mitsos, *Appl. Energy* **2018**, *231*, 757–767.
[102] BEIS, Greenhouse Gas Reporting: Conversion Factors 2020, **2020**.
[103] X. Zhang, C. Bauer, C. L. Mutel, K. Volkart, *Appl. Energy* **2017**, *190*, 326–338.
[104] G. Reiter, J. Lindorfer, *Int. J. Life Cycle Assess.* **2015**, *20*, 477–489.
[105] A. Sternberg, A. Bardow, *ACS Sustainable Chem. Eng.* **2016**, *4*, 4156–4165.
[106] Michael Carus, P. Skoczinski, L. Dammer, C. vom Berg, A. Raschka, E. Breitmayer, *Hitchhiker's Guide to Carbon Capture and Utilisation*, **2019**.
[107] K. Saravanan, H. Ham, N. Tsubaki, J. W. Bae, *Appl. Catal. B* **2017**, *217*, 494–522.
[108] B. R. de Vasconcelos, J. M. Lavoie, *Front. Chem.* **2019**, *7*, 392.
[109] P. Collet, E. Flottes, A. Favre, L. Raynal, H. Pierre, S. Capela, C. Peregrina, *Appl. Energy* **2017**, *192*, 282–295.
[110] T. McKone, D. Rice, T. Ginn, M. Bastani, A. Levy, A. Lenhart, B. A. Syz, R. Boudreaux, *California Dimethyl Ether Multimedia Evaluation. Tier I. Final Draft*, **2015**.
[111] K. Omata, Y. Watanabe, T. Umegaki, G. Ishiguro, M. Yamada, *Fuel* **2002**, *81*, 1605–1609.
[112] KOGAS DME Activities for Commercialization, **2011**.
[113] M. Bui, C. S. Adjiman, A. Bardow, E. J. Anthony, A. Boston, S. Brown, P. S. Fennell, S. Fuss, A. Galindo, L. A. Hackett, J. P. Hallett, H. J. Herzog, G. Jackson, J. Kemper, S. Krevor, G. C. Maitland, M. Matuszewski, I. S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D. M. Reiner, E. S. Rubin, S. A. Scott, N. Shah, B. Smit, J. P. M. Trusler, P. Webley, J. Wilcox, N. Mac Dowell, *Energy Environ. Sci.* **2018**, *11*, 1062–1176.
[114] C. Song, *Catal. Today* **2006**, *115*, 2–32.
[115] A. Goeppert, M. Czaun, J. P. Jones, G. K. Surya Prakash, G. A. Olah, *Chem. Soc. Rev.* **2014**, *43*, 7995–8048.
[116] W. Schakel, G. Oreggioni, B. Singh, A. Strømman, A. Ramírez, *J. CO_2 Util.* **2016**, *16*, 138–149.
[117] M. Tomatis, A. Mahmud Parvez, M. T. Afzal, S. Mareta, T. Wu, J. He, T. He, *Fuel* **2019**, *254*, 115627.
[118] KOGAS, KOGAS DME Activities for Commercialization, **2011**.
[119] Oberon Fuels, "Oberon Fuels," can be found under http://oberonfuels.com/, **2020**.
[120] C. Fernández-Dacosta, V. Stojcheva, A. Ramirez, *J. CO_2 Util.* **2018**, *23*, 128–142.
[121] P. Tundo, M. Selva, *Acc. Chem. Res.* **2002**, *35*, 706–716.
[122] M. Aresta, M. Galatola, *J. Cleaner Prod.* **1999**, *7*, 181–193.
[123] P. Kongpanna, V. Pavarajarn, R. Gani, S. Assabumrungrat, *Chem. Eng. Res. Des.* **2015**, *93*, 496–510.
[124] L. F. S. Souza, P. R. R. Ferreira, J. L. de Medeiros, R. M. B. Alves, O. Q. F. Araújo, *ACS Sustainable Chem. Eng.* **2014**, *2*, 62–69.
[125] J. G. M. S. Monteiro, O. de Queiroz Fernandes Araújo, J. L. de Medeiros, *Clean Technol. Environ. Policy* **2009**, *11*, 459–472.
[126] I. Garcia-Herrero, R. M. Cuéllar-Franca, V. M. Enríquez-Gutiérrez, M. Alvarez-Guerra, A. Irabien, A. Azapagic, *ACS Sustainable Chem. Eng.* **2016**, *4*, 2088–2097.
[127] V. Spallina, I. C. Velarde, J. A. M. Jimenez, H. R. Godini, F. Gallucci, M. Van Sint Annaland, *Energy Convers. Manage.* **2017**, *154*, 244–261.
[128] F. M. Mota, D. H. Kim, *Chem. Soc. Rev.* **2019**, *48*, 205–259.
[129] P. Jiang, A. M. Parvez, Y. Meng, M. xia Xu, T. chi Shui, C. gong Sun, T. Wu, *Energy* **2019**, *187*, 115933.
[130] H. Yang, C. Zhang, P. Gao, H. Wang, X. Li, L. Zhong, W. Wei, Y. Sun, *Catal. Sci. Technol.* **2017**, *7*, 4580–4598.
[131] CarbonNext, Deliverable 4.3: Economic and Environmental Impacts of Most Promising CCU Pathways, **2018**.
[132] R. Cuéllar-Franca, P. García-Gutiérrez, I. Dimitriou, R. H. Elder, R. W. K. Allen, A. Azapagic, *Appl. Energy* **2019**, *253*, 113560.
[133] C. van der Giesen, R. Kleijn, G. J. Kramer, *Environ. Sci. Technol.* **2014**, *48*, 7111–7121.
[134] L. E. Hombach, L. Doré, K. Heidgen, H. Maas, T. J. Wallington, G. Walther, *J. Cleaner Prod.* **2019**, *207*, 153–162.
[135] Y. Li, L. Li, J. Yu, *Chem* **2017**, *3*, 928–949.
[136] G. Centi, S. Perathoner, *Catal. Today* **2020**, *342*, 4–12.
[137] R. Peters, M. Baltruweit, T. Grube, R. C. Samsun, D. Stolten, *J. CO_2 Util.* **2019**, *34*, 616–634.
[138] M. Bailera, P. Lisbona, L. M. Romeo, S. Espatolero, *Renewable Sustainable Energy Rev.* **2017**, *69*, 292–312.
[139] P. Goglio, A. G. Williams, N. Balta-Ozkan, N. R. P. Harris, P. Williamson, D. Huisingh, Z. Zhang, M. Tavoni, *J. Cleaner Prod.* **2019**, *244*, 118896.
[140] A. Shulenberger, F. Jonsson, O. Ingolfsson, K.-C. Tran, *Process for Producing Liquid Fuel from Carbon Dioxide and Water*, **2007**.
[141] International Organization for Standardization (ISO), *ISO 14040:2006*, **2006**.
[142] A. Zimmermann, L. J. Müller, A. Marxen, K. Armstrong, G. Buchner, J. Wunderlich, A. Kätelhön, M. Bachmann, A. Sternberg, S. Michailos, H. Naims, P. Styring, R. Schomäcker, A. Bardow, *Techno-Economic Assessment & Life-Cycle Assessment. Guidelines for CO2 Utilization*, **2018**.
[143] N. von Der Assen, J. Jung, A. Bardow, *Energy Environ. Sci.* **2013**, *6*, 2721–2734.
[144] CarbonNext, Deliverable 4.2: Methodology to Assess the Environmental Impact and Energy Efficiency of CCU, **2018**.
[145] S. Michailos, P. Sanderson, A. Villa Zaragoza, S. McCord, K. Armstrong, P. Styring, F. Mason, G. Stokes, E. Williams, A. Zimmermann, J. Wunderlich, G. Buchner, R. Schomäcker, L. Müller, A. Bardow, A. Bardow, A. Marxen, H. Naims, *Methanol Worked Examples for the TEA and LCA. Guidelines for CO2 Utilization*, **2018**.

Manuscript received: September 8, 2020
Revised manuscript received: November 20, 2020
Accepted manuscript online: December 13, 2020
Version of record online: January 5, 2021

© 2020 The Authors. ChemSusChem published by Wiley-VCH GmbH