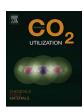
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Non-fossil CO2 recycling—The technical potential for the present and future utilization for fuels in Germany



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ABSTRACT

Apart from its negative effects on the climate, CO_2 is also a valuable resource, containing carbon – one of the most used and processed elements on Earth. Today, more than 30 Gt of CO_2 is emitted each year, with an increasing tendency. Of this, the main share results from the burning of fossil fuels; only a small fraction derives from renewable fuels. In this study the renewable sources of CO_2 are examined in terms of their current, nearterm (2030) and long-term (2050) potential. Current and potential future market output is based on a literature review concerning the future energy market and policy frameworks. As a reference for the utilization of CO_2 , three promising fuel options (methanol, methane and future Fischer-Tropsch fuels) are investigated. Along with the production capacities, H_2 demand for the conversion was calculated on the basis of chemical process simulations. One aim of this study was to provide a comprehensive overview of the expected range of CO_2 recycling from non-fossil sources. It was found that quantities of non-fossil CO_2 lie far behind fossil CO_2 quantities (6.8% of fossil CO_2 provision in 2015). However, with rising demand for CO_2 -based products and a concurrent decrease in the amount and willingness to use fossil CO_2 , in the future non-fossil CO_2 will grow in importance (reaching up to 23% of fossil CO_2 provision in 2050). The study shows that CO_2 from non-fossil sources is a reliable and available source of carbon.

1. Introduction

Climate change is seen as a very demanding challenge in the 21 st century [1]. CO_2 is not only a greenhouse gas but also a potential source for building organic materials with a hugh potential.

Currently, $32.3\,\text{Gt/a}$ of CO_2 are emitted per year globally (2015) [2,3]. It is expected that if no countermeasures are undertaken, the rate of CO_2 emissions will further increase. To stay within the limited global warming target of $1.5\,^{\circ}\text{C}$, emissions from 2017 on must be limited to a cumulative sum of 700 GtCO_2 until 2100 [3].

Typical sources for CO₂ are power generation (fossil and bioenergy), as well as heavy industry (e.g. the production of construction materials) and transport. At present, approximately 27 Gt/a are emitted from fossil plants (coal and gas), which constitute 76% of total CO₂ emissions (globally). The second largest emitter, with approximately 8 Gt/a (22%), is the heavy industry (mainly cement and steel production). In

2015, Germany emitted 0.79 Gt, approximately 2.5% of global emissions. The major part of these emissions are emitted in the form of exhaust gas and of this, only a minor fraction, or about 2% (0.7 Gt $\rm CO_2$ per year, globally), is highly concentrated $\rm CO_2$ that is suitable for direct processing [4]. In this context, the question arises of what amount of $\rm CO_2$ can be (sustainably) utilized for reuse and/or permanent/temporarily stored.

Therefore, the first part of this study is dedicated to the potential ${\rm CO_2}$ sources and amounts (from today until 2050) with regard to sustainable utilization.

For CO_2 emitting sources the focus is on those with a high potential. High potential sources are those that emit CO_2 at higher concentrations and that will likely still be present in 2050. Additionally, a focus will be placed on sources from waste streams. From our perspective, these are mainly biogenic processes and CO_2 from the cement industry, where no alternatives are yet within reach. Important within the biogenic

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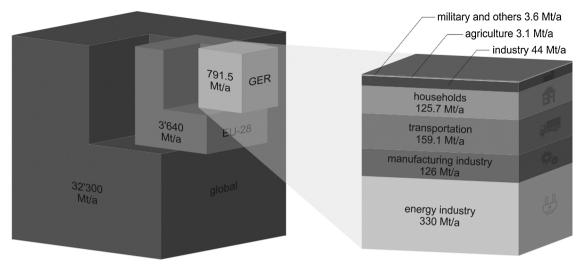


Fig. 1. Global anthropogenic CO2 emissions (correct proportions) (left) and German CO2 in 2015 by sector (right).

processes, as well as for CO₂ from the cement industry, the CO₂ must be captured in an environmentally-friendly and economically-feasible manner. Due to the lack of data on the emitted CO₂ amounts from these pathways, one aim of this study is to provide this data. Furthermore, we will evaluate in which relation the CO₂ from biogenic processes towards the CO₂ from fossil-based processes is stated. Thereby, we focus on the CO₂ that is separated during the biochemical conversion. Additionally, we look for potential CO₂ from the cement industry, where large amounts are emitted but currently remain unused. The emission of CO2 during cement production results in large amounts from the lime production which, even with high optimization efforts, cannot be avoided (chemical reaction within the lime production). Moreover, by assuming to substitute the thus far used fossil fuel by a renewable one (e.g. biochar), CO₂ from the cement industry can be regarded as a non-fossil future carbon source. Thus, CO2 utilization for the production of chemicals seems promising in terms of CO2 reduction targets.

The second part of this study explores possible conversion pathways of the available CO_2 . The possibilities of carbon capture and utilization (CCU) are very diverse. CO_2 is a nontoxic and non-flammable resource that can be either directly used (e.g. as dry ice or inert gas or within the chemical industry as a feedstock, amongst other applications) or for bulk chemicals such as methanol, acetic acid or formaldehyde. If emitted CO_2 (i.e. from combustion) is captured and utilized, it contributes to CO_2 reduction in the atmosphere by means of a reuse cycle.

Within our study we focus on CCU in the chemical industry. To achieve this, we will give an overview of possible applications and indicate the most promising approaches. Furthermore, the theoretical amount of $\rm H_2$ necessary for conversion into chemicals was calculated. As a study area, Germany and estimate the available non-fossil $\rm CO_2$ today and in future (2030 and 2050) was chosen.

2. Process CO₂ sources

To limit and reduce the amount of CO_2 emissions into the atmosphere, different options are available. If measures for the prevention of CO_2 emissions have been exhausted, the capture and utilization of CO_2 (CCU) is one further option. Centralized point sources with already high concentrated CO_2 are, in general terms and economically-speaking, more efficient due to cost savings from unnecessary CO_2 concentration units than decentralized, small-scale units. However, decentralized small-scale sources are also relevant for CCU technologies regarding a holistic approach.

This section of the paper describes current and future quantities of process CO₂ in Germany. Hence, conventional (i.e. fossil power generation and the construction industry) as well as renewable (e.g.

biomass) sources are evaluated. The focus of this paper is on non-fossil CO_2 . The emissions from fossil power generation and the construction industry are shown to illustrate the gap between non-fossil and conventional CO_2 potential, and in the case of the cement industry, where CO_2 emissions are immanent to the production process. Within this range, the process CO_2 generated by the construction industry can be regarded as sustainable if the possible input energy for the process is sustainable (e.g. biochar or waste streams).

The steel industry, one of the major CO_2 -emitting industries, is not considered in this study. Currently, fossil oil, gas and coal are used to produce steel. Unlike the cement industry, there is a CO_2 -free operation mode to produce steel [5,6]. The present day use of fossil fuel can be completely substituted by H_2 derived from renewable energy. This is technically feasible, as several studies have proven. Similar studies investigating CO_2 sources have also found the steel industry to be a depleted CO_2 source by 2050 [7]. By implication, in such a scenario the necessary amount of renewable energy must be provided, which corresponds to economic barriers. To address these would be beyond the scope of this study, and therefore we refer to other studies [5].

All the necessary data considered in this study were collected by official publication databases or calculated on that basis.

2.1. Emissions for CO₂ from fossil sources

For decades, there has been an increase in energy consumption, combined with an increase in CO_2 emissions; a countervailing trend is currently not observable [8]. Current global yearly anthropogenic CO_2 emissions are 32.3 Gt/a (2015) [2]. These emissions mainly originate from the power, transportation and manufacturing industries. In Fig. 1, global anthropogenic CO_2 emissions are illustrated. With 3.64 Gt/a (2015), the EU contributes contribute approximately 11% to global emissions and thus are a leading CO_2 producers [9]. Germany emitted 0.79 Gt, approximately 22% of all EU-28 emissions in 2015, and is therefore the leading emitter in the EU (followed by the U.K. and France) and is at rank 6 in the world [10].

For Germany, the greenhouse gas emissions are shown in more detail in Table 1. The total emissions ($CO_2 + CO_2$ equivalents) in the year 2015 were $\tilde{}$ 887.4 Mt without LULUCF (land use, land use change, forestry) [10].

The majority of greenhouse gas emissions are caused by CO_2 (~88%), followed by methane and nitrous oxide. From 1990 until today, there was a steady decrease in CO_2 emissions, with a slowed reduction rate in recent years. To evaluate the theoretically possible amounts of CO_2 for utilization, the following restrictions were applied to national trend tables for the German atmospheric emission [10]:

Table 1 Fossil CO_2 emissions in Germany for potential CCU processing, historic and present state (2015) [10].

year	1990	2000	2010	2015
unit greenhouse gas emissions (incl. CO ₂ - equivalent)	Mt _{CO2} /a 1219.6	Mt _{CO2} /a 1,005.0	Mt _{CO2} /a 925.4	Mt _{CO2} /a 887.4
total CO ₂ emissions	1,052.2	899.3	832.4	792.1
energy (total)	989.8	839.5	784.2	744.3
energy industries*	423.9	354.6	351.7	330.0
Manufacturing industries*	185.1	129.0	124.2	126.0
Other	380.8	355.9	308.3	288.3
industry and product use (total)	59.3	57.0	45.9	44.7
mineral industry*	22.8	22.3	18.4	18.7
chemical industry*	8.1	8.4	8.3	5.6
metal industry*	25.1	23.5	16.4	17.9
other	3.3	2.8	2.8	2.5
sum of CO ₂ for CCU	655.0	537.8	519.0	498.2

All values are for CO_2 only, excluding LULUCF, no aviation, no biomass. Data source, categories 1.A.1.1, 1.A.1.2, 2.A, 2.B, 2.C, according national trend tables by UBA, resp. European Environmental Agency.

- * Suitable for CCU.
- Direct CO₂ (no CO₂-equivalent emissions)
- (High) concentrated point sources (e.g. the energy and mineral industries), no transport

 ${\rm CO_2}$ emissions account for 86–90% of all greenhouse gas emissions, with an increasing share. ${\rm CO_2}$ equivalents consist mainly of CH₄, N₂O, hydrofluorocarbons (HFC) and perfluorocarbons (PFC) and are highly harmful in terms of the greenhouse gas effect, but are unsuitable for CCU, and therefore will not be further considered.

The main source of CO_2 is fuel combustion within the energy branch (energy industry, as well as the manufacturing industry), see also Fig. 1. A further major CO_2 emitter is the transport sector (~15%), but due to its decentralised nature it is not suitable for carbon capture. The mineral, chemical and metal industries, where CO_2 is often emitted as a chemical by-product (e.g. the cement industry), accounted for ~5% of global CO_2 emissions from 2015. Of the total CO_2 emissions, that which would be theoretically suitable for CCU constitute a CO_2 share. Additionally, further restrictions (e.g. economic reasons, scale) limit the total amount of available CO_2 .

Predicting future CO_2 production is no trivial task. Several studies have been conducted with a wide range of assumptions and scenarios [11–15]. The forecasts range from a low decrease, mainly in the so-called reference scenarios with little change of current behaviour/policy/infrastructure to highly decrease the respective reduction scenarios with up to 80% and even 95% GHG reduction by 2050 against 1990 levels. Table 2 provides an overview of the results of two of these studies. In these cases, the remaining CO_2 emissions are emitted by the agriculture and manufacturing sectors. The calculations of these studies are based on a wide variety of assumptions, such as innovative future processes in energy production, a shift in transportation systems, highly improved housing insulation, and so forth. Thus, they show a high degree of uncertainty. Furthermore, they often do not give detailed values for all sectors, but rather a broader overview.

The energy and manufacturing industries were identified as possible point sources for CCU. It can be shown that with a policy targeting 80% $\rm CO_2$ reduction by 2050, in 2030, 50–78% fossil $\rm CO_2$ and in 2050 13–23% of theoretical fossil $\rm CO_2$ for CCU processes are available, with a decreasing share. However, this $\rm CO_2$ is fossil-based and a further decrease is highly likely under optimistic scenario assumptions.

2.2. CO₂ potential from the construction industry

Emitting a total of around 19 million tons of CO₂ a year, the German cement industry makes a significant contribution to anthropogenic

Table 2 Fossil CO_2 emissions in Germany for potential CCU processing, 2030 and 2050, aiming for an 80% CO_2 reduction target [11,15].

year	2030	2050	2030	2050
unit source	Mt _{CO2} /a	Mt _{CO2} /a	Mt _{CO2} /a	Mt _{CO2} /a
greenhouse gas emissions (incl. CO ₂ -equivalent)	552.3	209.2	447	157
total CO ₂ emissions	497*	188*	387	117
energy	404*	116 *	262	67
energy industries	169*	31*	n.d.	n.d.
manufacturing industries	78 [*]	34*	n.d.	n.d.
heavy industry and product use (mineral, chemical and metal industry)	n.d.	n.d.	37	10
sum of CO ₂ for CCU	247*	66*	< 387	< 117

n.d. - no data

greenhouse gas emissions [16–18](VDZe.V.ÉÉ. These emissions are distributed amongst 53 cement plants in Germany, of which 18 do not have integrated clinker production. The highest regional concentration is located in the northern part of North Rhine-Westphalia (Ruhrgebiet) [19].

The $\rm CO_2$ emissions, incidental to the cement production, can be assigned to three different sources: electricity-related (~13%), thermal energy-related (17%) and chemical reaction-related (70%) [20]. The major share of chemical reaction-related emissions is due to the calcination reaction of calcium carbonate (CaCO₃) to produce clinker (CaO), shown in reaction Eq. 1 [10].

$$CaCO_3 \leftrightarrow CaO + CO_2$$
 (1)

The clinker produced with around 70 mass-% – depending on cement quality [21] – accounts for the largest component of cement.

Since most CO_2 emissions are due to the immanent reactions that take place during clinker production, the only possibility to significantly reduce emissions in the cement industry is by means of CO_2 sequestration [22].

For instance, the CEMCAP project [23] is dedicated to researching ${\rm CO}_2$ capture from cement plants. For this purpose, several different ${\rm CO}_2$ capture technologies suitable for integration into cement production are assessed theoretically as well as experimentally, namely amine scrubbing, the oxyfuel process (as a full and partial concept), membrane-assisted liquefaction, chilled ammonia process (CAP) and calcium looping (CaL). The goal of this project is to raise the TRL (technology readiness levels) of these capture technologies to at least 6. Furthermore, all technologies should be analysed in a techno-economic manner to decide which technologies are most suitable and promising for implementation in existing or future cement plants. [24]

In the following, the technical potential for the sequestration and utilization of CO_2 from the German cement industry will be assessed. The technical potential is the amount that can be obtained with reasonable technical effort, while the economic potential lies within the technical potential and is restricted by economic constraints.

2.2.1. Future CO2 potential

To evaluate the potential for CO_2 sequestration and utilization in the cement industry, an inventory of the current emission status will first be made. The European Pollutant Release and Transfer Register (E-PRTR) requires that all pollution sources of air, water or soil exceeding a certain limit report their yearly emissions based on standardized measurements or calculation methodologies [25]. For CO_2 emissions, all facilities with emissions above $100 \, \rm kt_{CO2}/a$ are required to report. According to the E-PRTR, the total amount of CO_2 emitted by cement production plants in 2015 totals $24.63 \, \rm Mt_{CO2}$. In contravention of the

 $^{^{*}}$ Assumption: 10% of all CO $_2$ equivalent emissions originate from non – CO $_2$ gases (2015 value).

Table 3Development of production rates relating to the cement industry in Germany [15].

	2010	2020		2030		2040		2050	
	Total	Production	rate	Production	rate	Production	rate	Production	rate
	[kt]	[kt]	[% ₂₀₁₀]	[kt]	[% ₂₀₁₀]	[kt]	[% ₂₀₁₀]	[kt]	$[\%_{2010}]$
Clinker calcination	22,823	21,036	-7.8	18,617	-18.4	16,572	-27.4	14,697	-35.6
Limestone processing	24,311	22,214	-8.6	21,017	-13.5	20,067	-17.5	19,157	-21.2
Cement grinding	32,721	30,715	-6.1	29,420	-10.1	28,433	-13.1	27,470	-16.0

numbers given by the cement industry [18], only 49 sites have been reported (due to the 100 kt/a threshold). This also includes $\rm CO_2$ emissions derived from biomass or other alternative fuels for electricity or heat production on-site, which are not accounted for in the aforementioned value of 19 Mt $_{\rm CO_2}$ /a. However, these sustainably-derived $\rm CO_2$ sources are also of interest for further utilization.

In the next step, a prognosis for the development of these CO_2 potentials in the future will be made. This requires the answering of two crucial questions: How will the production rates of cement in Germany change over the course of the coming years? How much CO_2 will be released in the production process per ton of cement?

Assumptions for the former can be made by looking into development scenarios. Pflugner et al. [15] provide a comprehensive description of development scenarios for the modelling of future climate protection plans for the German government. These scenarios are based on assumptions for economic and social development and discussed by executive-level representatives of politics, society and industry. Table 3 gives an overview of the assumed rates of production for materials related to the cement industry.

To answer the latter question, the most important technological research advancements in the sustainable production of cement should be considered and assessed. Since 70% of CO_2 emissions in cement production are immanent to the calcination reaction, as described above, only the residual share is accessible for emission reduction by innovative technologies. This comprises heat and electricity production.

Already today, alternative technologies are integrated into the production of heat to achieve reductions of CO_2 . The primary measure for CO_2 reduction in the cement industry is the use of alternative fuels in the furnace for supplying process heat, which currently holds a share of 65% (with the predominant share being industrial waste materials or tires). Despite the fact that CO_2 from the burning of waste material and biomass is not accounted for in the balancing of greenhouse gas emissions, its sequestration and utilization is still possible. Furthermore, the possibility of supplying process heat by means of the direct integration of thermal solar energy has been investigated [26,27]. Although the first experiments have proven the feasibility of this approach, its application is only economical in regions with high direct solar radiation, such as southern Europe or northern Africa.

In theory, all electricity used in cement production could already be provided by renewable sources today. Considering the fact that the electricity is not generated on-site, this does not have an effect on the amount of available CO₂.

Table 4 shows the assumptions for CO₂ emitted and available for utilization at the sites of cement production for the considered years of 2030 and 2050 compared to current values, selected for further analysis

in this paper. The downward correction for the recession of total cement production was assumed to be $15\%_{2010}$ for 2030 and $25\%_{2010}$ for 2050 based on the trends of production shown in Table 3, above. Additionally, the quantities are reduced to account for measures of CO_2 reduction. For this, reduction values of $5\%_{2010}$ for 2030 and 2050 are chosen, as specific CO_2 emission values for cement production have nearly stalled in the past years [20]. The last columns show the amount of CO_2 available for utilization, with an assumed capture rate of 90%, which is feasible with today's state of the art technologies [28]. As a reference value for future development, the value for 2015, as reported by the E-PRTR [25] is given.

These values state the technical potentials for the utilization of CO_2 emitted by the cement industry. Another downward adjustment must be made when considering economic feasibility. From a technical point of view, all of these sites are suitable for sequestration and the further processing of CO_2 . However, an economic analysis of CO_2 sources is beyond the scope of this paper.

2.3. CO₂ potential from biomass

Regarding the sustainability and long term perspective, renewable sources of CO_2 are evaluated within this study. Typical renewable sources of CO_2 are the biochemical conversion (biogas/biomethane pathway) and thermochemical conversion (gasification and methanation pathway) of biomass. In this study, we focus on the commodity potential of CO_2 from biochemical conversion, which is already well-established in the market.

The biogas/biomethane process shows high potential for future CO₂ capture and utilization. The typical biogas process consists of substrate pre-treatment (mainly crushing), fermentation (anaerobe digestion) and a post-treatment (mainly the removal of sulphur compounds like H₂S). The produced biogas is a mixture of mainly methane and CO₂, while methane is commonly the major part, constituting between 50% and 70% [29]. The biogas can either be used directly within a CHP process (combined heat and power) or upgraded to biomethane [30]. The typical bio-SNG (synthetic natural gas) process of thermochemical conversion is based on substrate pre-treatment (mainly crushing and drying), gasification, syngas treatment, methanation and upgrading [31]. The products of biomethane and bio-SNG are chemically identical (pure methane) and can be used as a substitute for natural gas. Within the upgrading process of both pathways (biogas/biomethane and bio-SNG), the CO₂ is separated as a by-product. Depending on the upgrading technology, it is diluted with air or is highly concentrated. While the biogas and biomethane processes are already established in the market, the bio-SNG process is still at the research and demonstration stage [32].

Table 4Assumptions for the development of future CO2 emissions by cement production.

2015		2030		2050		
Total emissions [25]	Available CO ₂ after capture [90%]	Total emissions after corrections [-5%; -15%]	Available CO ₂ after capture [90%]	Total emissions after corrections [-5%; -25%]	Available CO ₂ after capture [90%]	
Mt _{CO2} / a 24.63	Mt _{CO2} / a 22.17	Mt _{CO2} / a 19.70	Mt _{CO2} / a 17.73	Mt _{CO2} / a 17.24	Mt _{CO2} / a 15.12	

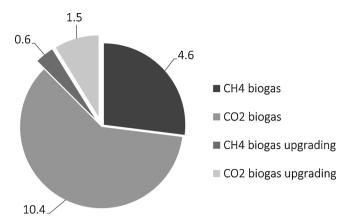


Fig. 2. CH_4 and CO_2 (in Mt) quantities of biogas and biogas upgrading in Germany for 2016.

In Fig. 2, the CH₄ and CO₂ quantities from biogas and biogas upgrading to biomethane in Germany are plotted. The values are based on own calculations derived from data 2016. It assumes a total availability of the whole CO₂ fraction within the biogas and biomethane pathway. This includes all biogas upgrading (193) and biogas plants (9016) in Germany [33–35]. In total, they have a combined CH₄ and CO₂ stream of approximately 13.4 bil m³/a. To gather this amount, the streams of all biogas upgrading plants and those of all biogas plants (if they would be converted to biogas upgrading plants) would need to be captured. Thus, this amount is the theoretical maximum capacity that could be gathered. On the basis of this assumption, there is a potential of 10.4 Mt CO₂ from biogas plants and 1.5 Mt CO₂ from biogas upgrading plants for 2016. Whereas the CO₂ from biogas upgrading is separated from the methane by default, the CO₂ from the biogas plants is, thus far, not separated and available.

2.3.1. Future CO2 potential

In Germany, the majority of bioenergy plants profit directly or indirectly from the Renewable Energy Sources Act and within regulated feed-in tariffs. Generally, tariffs are granted for 20 years. If no profitable operation is achieved after this funding period, a shutdown of the plants

is likely. Scheftelolwitz and Thrän predict that for the existing biogas and biogas upgrading plants, consistent energy production (and thus CH_4 and CO_2 provision) at the current level until approximately 2024 [36]. From this point on, a steady and fast decrease commences and ends in 2034 with biogas and biomethane plants stopping respectively operate if no countermeasures are implemented. From the present state until 2024, no decrease of CO_2 for CCU can be assumed, followed by a likely strong decrease by 2034. It must be kept in mind that these scenarios apply if no counter-mechanism for the biogas plant shutdown, like further subsidies or new market models, are applied. Within this study, the possible CO_2 availability is evaluated by implying an optimistic biogas/biomethane future for Germany, primarily based on waste as biogas/biomethane substrate.

Some scenario conditions for waste stream-focused biogas/biomethane production until 2050 are as follows:

- O A consistent number of biogas plants until 2024 (status quo)
- A light increase in the number of biogas upgrading plants through 2024 (extrapolated trend)
- A positive political framework for biogas and biomethane plants based on waste streams
 - Exploitation of the potential biomass resources (waste streams) until 2050
- Stagnation of energy crop-based biogas and biomethane plants through 2024
- Between 2024 and 2034, the shutdown of energy crop-based plants to zero, a continuation of 90% of all existing biogas plants that are already based on waste streams (10% of the waste stream plants are closed down due to missing reinvestment)
- Potential biomass resources according to [37]
 - Biogas-relevant streams (thus far unused fractions) were applied in this study
 - Mainly manure and organic waste from kitchens, canteens, weekly markets as well as cereal straw
 - In total, between 16 and 20.5 Mt sof biomass (dry matter), technical potential
- Assuming a constant amount of waste streams through 2050
- Exploitation of 50% of the average waste streams until 2050

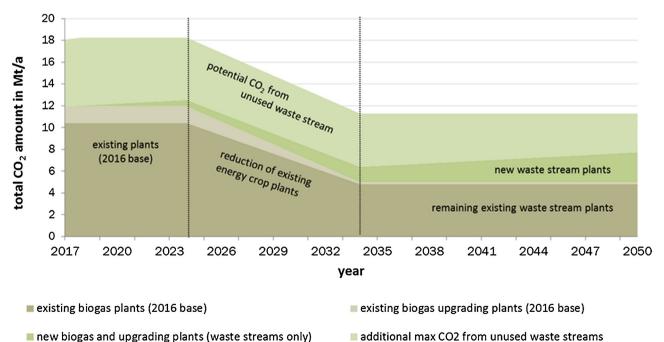


Fig. 3. Development of CO₂ (in Mt) from biogas and biogas upgrading through 2050.

• 9.1 Mt (dry matter)

Fig. 3 displays the development of the total available CO_2 stream from biogas and biogas upgrading plants between 2017 and 2050. From 2024 through 2034 is a strong decrease of CO_2 , from 12 to 6 Mt, due to the shutdown of energy crop-based plants. Under the chosen scenario conditions, the new waste stream-based plants are unable to compensate for the loss. In 2050, the total CO_2 amount accumulates to around 8 Mt. However, the total potential (including a still unused waste stream) is 16.1 (2030) and 11.3 Mt/a (2050) and thus was almost as high as in 2017 with energy crops still in use.

3. CCU technologies

3.1. Technology overview

CCU technologies have been developed for almost 50 years. The main driver initially was the oil crises in the 1970s. However, as a result of the need to avert climate change and the shift from fossil to sustainable energy resources, research into these technologies has gained a new impetus [38].

On the basis of a comprehensive literature review, possible *CCU* pathways were collected, allocated into categories, their TRLs estimated and the possible market share of the products calculated.

The categories were divided by the type of utilization (direct or for further synthesis). For the synthesis pathways, further sub-divisions, such as biological and chemical processes, as well as the different chemical reaction types, such as Sabatier- or water-gas-shift reactions, were introduced. Fig. 4 provides an overview of the pathways.

The biological group of CCU processes is mostly based on different algae and bacteria types. Within these biogenic processes, CO_2 is utilized in order to produce biomass, while some organisms also emit hydrogen during this process, such as cyanobacteria and green alga. [39].

More suitable for technologically mature processes are the chemical processes, which create substances that are chemically-identical to fossil-based ones. Most remarkable are the widely used products methane, methanol and hydrocarbons, which can easily be further processed and would therefore be very useful to the chemical industry. These processes for synthetically producing methane, methanol and hydrocarbons from $\rm CO_2$ are explained in detail in chapter 3.3. A rather new technology branch is the artificial photosynthesis, where the biological process serves as an example. The advantage of this kind of technologies lies in the direct utilization of sun light without bypassing processes [42,43]. However, the artificial photosynthesis is in an early stage of development and thus out of the scope of this study.

3.2. CCU market outlook

Currently, there is only little demand for CO_2 as a resource. Compared to the total global emissions (32.3 GT CO_2 in 2015), the potential CO_2 utilization is fairly limited. The most suitable sources for CCU are highly concentrated with a high volumetric flow rate, such as flue gas streams from power plants or cement facilities (compare Section 2).

The estimations in the literature for the yearly global demand of CO_2 as a feedstock for CCU vary. In a review of publications dealing with global CCU potential, Aresta et al. (2013) found that all range about the same maximum of 200 Mt CO_2 p.a. which are currently utilized [44–46]. Within these limits, the majority of this demand is synthesized into urea (58%), inorganic carbonates (25%) and methanol (4%). However, already today there is further demand in the direct utilization and CO_2 as a source for fuels or other materials. The share of direct utilization (e.g. beverage carbonization, food packing and industrial gas) is about 9%. Table 5 gives a detailed overview of the current and near term (within the next 10 years) demand of CO_2 as a resource. The near term demand was calculated with \sim 250 Mt [44,45], with the highest increase in the material branch. There are also studies

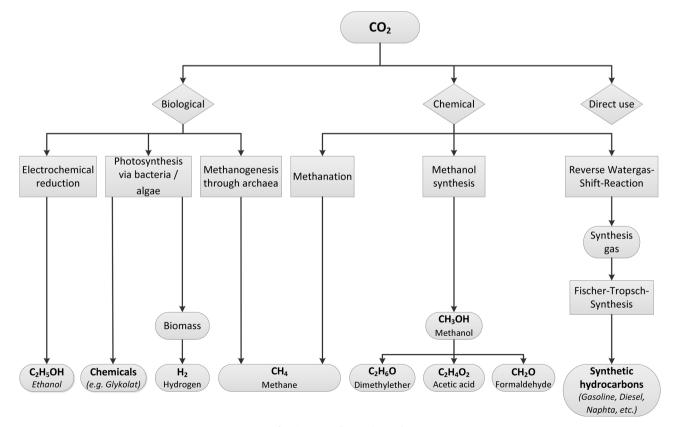


Fig. 4. CCU pathways [39-41].

Table 5 Global current and near term markets (estimated demand) for CO_2 (based on [44] and (Naims 2016)).

product/application	current est. volumes ^a		near term est. volumes ^b	
in Mt per year	CO_2	product	CO_2	product
direct utilization				
beverage	2.9	2.9	2.9^{d}	2.9^{d}
carbonization ^c				
food packing ^c	8.2	8.2	8.2^{d}	8.2^{d}
industrial gas ^c	6.3	6.3	6.3 ^d	6.3 ^d
materials				
urea	114.0	155.0	132.00	180.0
inorganic carbonates	50.0	200.0	70.0	250.0
formaldehyde	3.5	21.0	5.0	25.0
polycarbonates (PC)	0.01	4.0	1.0	5.0
carbonates	0.005	0.2	0.5	2.0
acrylates	0	2.5	1.5	3.0
carbamates	0	5.3	1.0	6.0
formic acid	0	0.6	0.9	1.0
polyurethanes (PUR)	0	8.0	0.5	10.0
fuels				
methanol	8.0	50.0	10.0	60.0
dimethyl ether (DME)	3.0	11.4	> 5.0	> 20.0
tertiary butyl methyl	1.5	30.0	3.0	40.0
ether (TBME)				
algae to biodiesel	0.01	0.005	2.0	1.0
total	197.4		249.8	

^a Current data is based on the 2013 estimates from [44].

that evaluate the long-term CCU demand. The most recent is from Assen, who predicts 1,500-2,000 Mt global yearly demand, mainly in the form of large-scale applications like CO_2 -based fuels [47]. According to these numbers, up to 6% of anthropogenic CO_2 could be captured and utilized within a constant loop of demand (based on 2015 CO_2 emissions).

On a regional level (for Germany), hardly any numbers are available. Patricio et al. (2017) evaluated the CO_2 demand for Europe by considering each country individually. For the year 2012, approximately $5\,\mathrm{Mt/a}\,CO_2$ demand were estimated for Germany, constituting the highest individual demand within the EU [46]. Fig. 5 compares German CO_2 demand (> $5\,\mathrm{Mt/a}$, based on Patricio et el. 2017) with the theoretical amount of non-fossil CO_2 from biogas and biogas upgrading plants. It can be seen that the theoretical CO_2 production surpasses twice the current demand in Germany for CO_2 .

The literature analysis of conventional output markets for possible CO₂-based products has shown a strong oversupply of CO₂ compared to product demands. For a technically- and economically-reasonable implementation of CCU products, novel market niches must be identified. A promising possibility is the market for chemical energy, as is used for

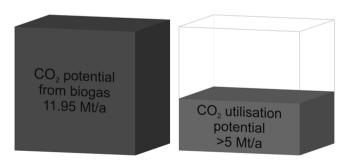


Fig. 5. Comparison of German CO₂ potential from biogas and biogas upgrading to CCU [46].

example in transportation fuels. This utilization pathway is analysed technically in the following chapter.

3.3. CO₂ utilization for the production of chemical energy carriers

Apart from the utilization of the captured CO_2 as a material resource, it is also possible to use it as a base resource in combination with hydrogen for the synthesis of chemical energy carriers. This pathway opens the possibility of producing a broad range of fuels for use in stationary as well as mobile applications. For reasons of scope, not all of the possibilities will be considered in this paper. Described as exemplary pathways, the three – technically and economically – most promising synthesis routes of methane-, methanol- and Fischer-Tropsch synthesis, will be described and evaluated.

For rating the processes at hand based on energetic performance, the efficiency factors described in the following will be used. These factors are specially derived for the rating of energy conversion in chemical processes and have been used in various publications [53–55]. The chemical conversion efficiency (η_{CCE}) only balances energy flows given by the reactant (H₂) and product (fuel). The plant efficiency (η_{plant}) balances all energy flows inside the synthesis plant. Therefore, in addition to the reactant and product energy flows, electrical (\dot{E}_{el}) and thermal energy (\dot{E}_{th}) demand for the operation of the plant are also considered. The energy flows of chemical streams are calculated via the mass flow (\dot{m}) and the lower heating values (LHV) of the respective stream.

Chemical conversion efficiency:

$$\eta_{CCE} = \frac{LHV_{fuel} \cdot \dot{m}_{fuel}}{LHV_{H_2} \cdot \dot{m}_{H_2}}$$
(2)

Plant efficiency:

$$\eta_{plant} = \frac{LHV_{Fuel} \bullet \dot{m}_{fuel}}{LHV_{H_2} \bullet \dot{m}_{H_2} + \dot{E}_{el} + \dot{E}_{th}}$$
(3)

3.3.1. Methanation

Methane is a very common energy carrier worldwide. It is the main component of most resources of "natural gas". The most common use of methane or natural gas in Germany is for the supply of heat in households. Also, natural gas power plants have gained an increasing share of Germany's power production mix due to their good dynamic characteristics compared to the predominant existing coal power plants. Furthermore, natural gas can be used in cars as a substitute for gasoline in Otto engines. Because of its higher H:C ratio, this technology has the potential to reduce direct CO_2 emissions in passenger cars in comparison to conventional gasoline or diesel fuel.

The production of methane on the basis of sustainably-produced $\rm H_2$ via electrolysis would therefore quickly find use in the existing infrastructure and markets.

Bailera et al. [56] compiled a list of existing power-to-gas projects and plants in 2017. The largest plant, in operation since 2013, is the Audi e-gas plant in the northern German town of Werlte. The plant operates with offshore wind, powering $3 \times 2.0 \text{ MW}_{el}$ alkaline electrolyzers. It is expected to produce around 1000 tons of methane per year [57].

Process description

The most prominent reactions taking place inside the methanation reactor are the following:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \Delta_R H^0 = -206.3 \, kJ/mol$$
 (4)

$$CO_2 + H_2 \leftrightarrow CO + H_2O \Delta_R H^0 = 41.2 \, kJ/mol \tag{5}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \Delta_R H^0 = -165.2 \, kJ/mol$$
 (6)

The actual quality of the reactions taking place in the reactor is dependent on pressure, temperature and the infeed ratio of the

^b Near-term data is based on the former 2016 estimates from [44] and includes CCU technologies that could be implemented within the next 10 years.

^c Data from IHS (2013), worldwide data without Latin America and Asia, except Japan.

^d estimated as constant by [45], not included in [44].

Table 6Energy and mass balance of the methanation process.

	Mass [kg]	Energy [MJ]
H ₂ CO ₂	0.502	60.1
CO_2	2.75	-
P_{el}	-	1.39
CH ₄	1	50

reactants. In practice, these reactions are always promoted by catalysts. Most existing applications of CO₂ methanation use nickel-based catalysts due to their good selectivity characteristics and the price stability of nickel [58].

As a reference process for the potential analysis, the methanation process designed, simulated and optimized by Baltruweit [59] will be described in the following.

The methanation reactions take place in two separate reactors to enhance the CO_2 conversion rate, the first being an isothermal reactor and the second an adiabatic one. Both operate at a pressure of 30 bar. After air cooling, gas entrance temperatures are 395 °C for the isothermal reactor and 350 °C for the adiabatic reactor. Downstream of the synthesis reactors, a product gas post-treatment process, consisting of CO_2 sequestration via amine scrubbing and gas drying via water vapor condensation, are connected. The described process yields a product gas composition of 5 vol.-% H_2 and 95 vol.-% of CH_4 , without the use of extensive gas conditioning processes. Table 6 contains an energy balance of the process from Baltruweit [59].

Based on Eqs. 4–6, the corresponding efficiency factors are:

$$\eta_{CCE,CH4} = 82.59\% \tag{7}$$

$$\eta_{plant,CH4} = 80.71\% \tag{8}$$

A literature review of power-to-fuel technologies conducted by Brynolf et al. [60] reports an efficiency range of 70–83%, in accordance with the results reported by Baltruweit [59].

3.3.2. Methanol

Similarly to methane, the use of methanol is widespread and versatile around the world. Part of the reason for this is that methanol can not only be used as an energy carrier, but also as the feed material for many chemical processes. This gives sustainably-produced methanol manifold opportunities for market implementation. The use of methanol as a transport fuel is not only possible, but already common practice, e.g. in China as an 85% drop-in fuel (M85) [61].

The conventional method of producing methanol is a chemical synthesis based on synthesis gas ($H_2 + CO$), which is mainly produced by means of steam reforming of natural gas, but can also be made via the gasification of coal or biomass. In the past years, numerous research projects have dealt with methanol synthesis from H_2 and CO_2 feedstock. The largest fully operating commercial power-to-fuel plant is the George Olah plant from CRI (Carbon Recycling International) in Iceland, which produces 5 million liters per year of climate-friendly methanol using geothermal power [62].

Process description

The methanol synthesis reaction based on CO_2 in Eq. 9 is commonly accompanied by the reactions in Eqs. 10 and 11:

$$CO_2 + 3H_2 \leftrightarrow H_3COH + H_2O\Delta_R H^0 = -130.98 \, kJ/mol$$
 (9)

$$CO_2 + H_2 \leftrightarrow CO + H_2O \Delta_R H^0 = 41.2 \, kJ/mol$$
 (10)

$$CO + H_2 \leftrightarrow H_3COH \Delta_R H^0 = -128.13 \, kJ/mol \tag{11}$$

As a reference, the process designed and simulated by Otto [63] will be described and assessed in the following. The synthesis reactions take place within an isothermal reactor under 250 °C and 80 bar. With a Cu/ $\rm ZnO/Al_2O_3$ catalyst system described by Pontzen [64] and a molar

Table 7Energy and mass balance of the methanol process.

	Mass [kg]	Energy [MJ]
H_2	0.188	22.55
H ₂ CO ₂	1.37	_
P_{el}	_	1.02
H ₃ COH	1	19.918

H₂:CO₂ ratio of 4, the CO/CO₂ conversion to methanol reaches a value of 36.9%. Through a liquid-gas phase-separation, nearly all of the unused CO₂ and CO can be recirculated. Table 7 shows the specific energy and material balance of the methanol synthesis. [63]

Eqs. 12 and 13 then yield the following efficiency factors:

$$\eta_{CCE,CH3OH} = 88.33\%$$
(12)

$$\eta_{plant,CH3OH} = 84.51\% \tag{13}$$

Brynolf [60] reports a range of 69–89% efficiency for methanol synthesis, based on a literature review, in accordance with the results given.

3.3.3. Fischer-Tropsch

Liquid hydrocarbons are considered an option for storing renewably generated energy. Due to their high volumetric energy density, liquid fuels are the main energy source for heavy load transportation, shipping, aviation, as well as long-distance traffic [65]. In the near future, the main transportation concepts will continue to be based on liquid hydrocarbons. The increasing amount of CO_2 in the atmosphere must also be taken into account. At this point, climactic changes due to excessive CO_2 content can only be countered with modern technological interventions. There are many different technologies applied for the production of chemicals from CO_2 . Amongst these, Fischer-Tropsch (FT) synthesis is the most prominent route to producing liquid fuels [66].

Process description

FT synthesis is a heterogeneously-catalyzed hydrogenation of CO with a polymerization character. Mainly liquid hydrocarbons are produced like diesel fuel, kerosene and gasoline [67]. Due to the catalytic process, the products of the synthesis are free of sulphur and produce less soot during combustion [68]. Thus, the diesel dilemma - soot or NO_x emissions – can be leveraged. Synthetic fuels can be used to fulfill EU6 standards. The catalysts used for the FT synthesis are typically Febased or Co-based. For the FT synthesis, the feed is synthesis gas in a composition of H₂/CO of slightly less than 2:1. Synthesis gas is conventionally provided through the steam reforming of natural gas. This process is called the gas-to-liquid (GtL) process. When solid biomass is gasified, instead of using natural gas as a feedstock, biomass-to-liquid (BtL) is the technical term. If CO2 and power are applied to producing liquid fuels, power-to-liquid is the relatively new wording [69,70]. All of these processes mainly differ in the generation of the synthesis gas (CO/H₂ mixture) and the adaptation of the right hydrogen to CO ratio.

When CO₂ is considered a carbon source, a two-step process typically combines reverse water gas shift (rWGS) and FT synthesis as a potential process combination. For the reduction of carbon dioxide, additional hydrogen is required apart from the hydrogen for FT synthesis. The hydrocarbons produced by the FT process are typically separated from unreacted feed and gaseous hydrocarbons and, finally, upgraded via hydrocracking and isomerization to obtain the final product.

In the rWGS reaction, CO_2 is converted into CO in accordance with the following equation:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \Delta H^{\circ}_{r298K} = 415 \text{ kJ/mol}$$
 (14)

The reaction is endothermic and therefore thermodynamically-favored at high temperatures. In the rWGS stoichiometry, the number of moles does not change; hence, the equilibrium composition is independent of the total pressure. However, methane can also be a byproduct depending on the nature of the catalyst, which may lead to even higher temperature requirements when increasing the pressure to avoid a higher methane equilibrium concentration. The Co-based FT synthesis is operated at pressures of 20–30 bars, and so a combined process reverse water gas shift (rWGS) and FT synthesis would have the advantage of less compression efforts for the complete system. Also, a process driven at higher pressures tends to reduce the size of the reactor. However, at higher pressure, this also bears the risk of increased carbon formation. The two competing reactions to rWGS, which are thermodynamically-favored at low temperatures and higher pressures are described by the following equations:

$$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O \Delta H^{\circ}_{r298K} = -206 \text{ kJ/mol}$$
 (15)

$$CO + 3H_2 \Leftrightarrow CH_4 + H_2O \Delta H^{\circ}_{r298K} = -165 \text{ kJ/mol}$$
 (16)

The underlying reaction in the FT synthesis can be summarized by the following simplified equation:

$$nCO + 2nH_2 \Leftrightarrow (-CH_2-)_n + nH_2O \Delta H^{\circ}_{r298K} = -n * 152 \text{ kJ/mol} (17)$$

The FT product, so-called 'syncrude', consists of a large variety of different species, as is mentioned above.

The chain growth probability in that polymerization process, and therefore the product distribution, depend on the catalyst type and reaction conditions. In the highly exothermic process, excellent heat dissipation in the FT reactor must be guaranteed to avoid local hot spots and chain termination due to desorption. Heat removal from the reactor is one of the major technical challenges of the FT process. As a consequence, conventional FT reactors like fixed bed, fluidized bed and slurry reactors must be equipped with efficient heat exchanger systems. The strengths and weaknesses of the different reactor designs are discussed in the work of de Klerk [66]. Conventional slurry-type FT reactors have in common that they are not load-flexible, as the dispersion of catalyst and gas is intolerant to fluctuation of the flow rates, as this might be required for PtL (power-to-Liquid) applications, in which feed is not constant over time. In a microstructured reactor with internal structures of up to 1 mm, a very high volumetric surface area for cooling is provided. Therefore, a highly compact and modular design can be realized for FT reactors in PtL processes [71]. With that reactor type, isothermal operation can be enabled, as well as the rapid adaptation of a changing feed and composition. As a consequence, microstructured reactors could be especially suitable for decentralized applications where dynamic conditions are applied. In Table 8 are displayed the energy and mass balances for a PtL plant [70].

The corresponding efficiency factors are calculated in accordance with [70]:

$$\eta_{\text{CCE,FT}} = 68.2\% \tag{18}$$

$$\eta_{\text{Plant,FT}} = 44.6\% \tag{19}$$

The application of micro-structured reactors in Fischer-Tropsch synthesis, allows the single pass conversion to be increased to 70% or even 80% [71], the effort for recycling or, more specifically, re-compressing the recycled gas to the FT synthesis pressure can be reduced quite effectively. Furthermore, the increased conversion is also

Table 8Energy and mass balance of Fischer-Tropsch.

	Mass [kg]	Energy [MJ]
H_2	0.533	96.682
CO_2	4.185	_
P_{el}	-	2.238
(-CH ₂ -) _n	1	44.121

associated with an increased chain growth probability due to the $\rm H_2/CO$ reduced ratio towards the reactor outlet [71], a gaseous byproduct is avoided. This, in turn, increases the overall product generation while reducing the losses of the carbon source. Energiedienst AG in Switzerland presented an overall plant efficiency of greater than 50% for electricity to fuel and more than 80% under consideration of additional use of the Fischer-Tropsch reaction heat for district heating in their planned 1 MW site at Laufenburg [72]. The synthesis plant shall be delivered by INERATEC GmbH [73].

4. Results & discussion

It has been shown that twice the current German CO_2 demand (~5 Mt) for CCU could be supplied by the CO_2 from biogas and biogas upgrading alone (~12 Mt theoretical amount, see Section 2.3). Additionally, ~22 Mt non-fossil CO_2 through the cement industry could be provided. Thus, the current production capacity of non-fossil CO_2 surpasses the current CO_2 demand. For a technically- and economically-reasonable implementation of CCU products, novel market niches must be found. A promising possibility is the market for chemical energy carriers, as are used, for example, as transportation fuels.

This study shows the high potential of the chosen CCU products (methanol, methane and Fischer-Tropsch fuels) combined with the related high $\rm H_2$ demand in Germany. These products were chosen because of the already well-established state of the art and good data available, while other technologies like the enzymatic reaction and artificial photosynthesis were not considered due to the early stage of development and lack of data, but are also a possible future pathway for CCU.

In Section 4.1, a detailed analysis of the related H_2 demand is conducted and evaluated. Concluding, Section 4.2 gives insight into the current markets for the chosen CCU products and evaluates its potential utilization for non-fossil CO_2 within this market.

4.1. Hydrogen demand

As is described above, hydrogen is necessary in order to produce methane, methanol or Fischer-Tropsch fuels from CO_2 . Within this study, the potential sustainable CO_2 in Germany today and for the years 2030 and 2050 has been calculated and analysed. For each technology process described in chapter 3.3, the resulting production potential (methanol, methane and Fischer-Tropsch fuels) were calculated, as well as the related H_2 demand, as is shown in Table 9. The conversions were then computed under the assumption of ideal conditions, while losses due to non-ideal reaction conditions were not considered.

For 2030 and 2050, the amount of CO_2 from biogas and biogas upgrading was merged due to higher uncertainties, which each process alone would have induced. Here, the total amount of biogas and biomethane, and thus of CO_2 , decreases through 2050 because of the assumed shutdown of energy crop-based plants (compare Section 2.3). Within the considered scenario, the installation of new plants (mainly based on organic waste as a substrate) cannot compensate for the decrease in capacity and CO_2 production. Regarding the cement industry, a decrease of capacity and CO_2 production due to process optimization can also be seen. Thus, non-fossil CO_2 sources, as well as fossil CO_2 sources, decreased from 2015 through 2050 (within the framework of an achievement of the Paris agreement).

As is shown in the table above, the largest production potential today arises from the cement industry, which therefore would require the largest amount of hydrogen. The sustainable and economic production of H_2 is one of the limiting factors to actually process sustainable CO_2 into methane, methanol and Fischer-Tropsch fuels.

The highest $\rm H_2$ demand is caused by methanation (0.18 kg per kg of $\rm CO_2$). The methanol production and Fischer-Tropsch fuel production show almost the same rate of $\rm H_2$ demand (0.14 kg of $\rm H_2$ per kg $\rm CO_2$ for the methanol process to 0.13 kg of $\rm H_2$ per kg of $\rm CO_2$ for the Fischer-Tropsch fuel).

Table 9
Production potential of methane, methanol and Fischer-Tropsch fuels (from sustainable CO₂) and the necessary amount of hydrogen for this purpose.

	2015		2030			2050			
	Biogas (CHP)	Biogas upgrading	Cement	Biogas (CHP)	Biogas upgrading	Cement	Biogas (CHP)	Biogas upgrading	Cement
CO ₂ availability [Mt]	10.4	1.5	22.2	16.1		17.7	11.3		15.1
Methane potential [Mt]	3.8	0.5	8.1	5.9		6.5	4.1		5.5
H ₂ demand [Mt]	1.9	0.3	4.1	3.0		3.3	2.1		2.8
Methanol potential [Mt]	7.6	1.1	16.1	11.7		12.9	8.2		11.0
H ₂ demand [Mt]	1.4	0.2	3.1	2.2		2.4	1.6		2.1
Fischer-Tropsch potential [Mt]	2.5	0.4	5.3	3.8		4.2	2.7		3.6
H ₂ demand [Mt]	1.3	0.2	2.8	2.1		2.3	1.4		1.9

(own calculations based on molecular weights [74,75]).

Table 10 Total amount of product and H₂ per conversion route.

	2015	2030	2050
CO ₂ availability [Mt]	34.1	33.8	26.4
Methane potential [Mt]	12.4	12.3	9.6
H ₂ demand [Mt]	6.2	6.2	4.8
Methanol potential [Mt]	24.8	24.6	19.2
H ₂ demand [Mt]	4.7	4.6	3.6
Fischer-Tropsch fuel potential [Mt]	8.1	8.1	6.3
H ₂ demand [Mt]	4.3	4.3	3.4

Table 10 summarizes the total amount of product and related $\rm H_2$ demand per conversion route. If all of the available $\rm CO_2$ (from biochemical as well as cement production) were already used today for the synthesis, 4.3–6.2 Mt $\rm H_2$ would be necessary, depending on the chosen utilization pathway, or a combination of them. Considering the mass flow rates, the highest amount can be produced via methanol, followed by methane and Fischer-Tropsch.

For comparison, Robinius et al. [76,77] discussed a scenario in which by the year 2050, roughly 4 to 6 Mt of hydrogen can be produced via electrolysis from surplus of renewable energy sources. Furthermore, it was shown that a dedicated hydrogen infrastructure to supply the demand is economically feasible [78].

4.2. Comparison with output markets

For the products chosen for this study, the yearly demand in Germany and related market turnover were determined (see Table 11). The market turnover is calculated on the basis of the product demand and average market price.

For reasons of simplification, methane was put on level with natural gas, whose main component is methane. For the future Fischer-Tropsch fuels gasoline, diesel and kerosene were chosen as the represented hydrocarbons. These were also the fuels that were evaluated in Section

Table 11
Demand, market price and market turnover in 2015 in Germany for methanol, methane and future Fischer-Tropsch fuels (selection) [79–85].

	2015		
	yearly demand in Mt	price in €/t**	turnover in bil. €
Methane	77.2	317	24.5
Methanol	0.94*	342	0.32
Future Fischer-Tropsch			
fuels			
Gasoline	18.9	1,864	35.3
Diesel	36.8	1,393	51.3
Kerosene	8.5	452	3.8

^{*} Production capacity in Germany.

3.3.3.

Due to a lack of data, no national demand for methanol be evaluated. However, the yearly production of methanol in Germany is around 0.94 Mt in 2015 [86], which indicates a large national market. With costs of ϵ 342 per ton of methanol, this resulted in a turnover of 321 mil. EUR in 2015.

In 2015, the yearly demand of methane was around 77.2 Mt. Thus, if all the here evaluated and available CO_2 from biogas and cement were to be converted to methane, around 16% of fossil-based methane could be replaced with non-fossil product. Therefore, synthetic methane alone cannot function as a substitute for fossil methane. The same conclusion can be drawn for the Fischer-Tropsch fuels. The substitution of these fossil-based products with products based on non-fossil CO_2 is not an adequate solution alone. It must go along with decreasing consumption and possible other substitutes to meet the targeted GHG emission savings.

In contrast to methane and FT fuels, methanol has a much lower consumption-respective production rate in Germany. The non-fossil CO_2 produced through methanol could substitute German production several times over. It must be kept in mind that for this scenario, the CO_2 from highly decentralized point sources must be collected and utilized, and this relates to thus far unknown costs. In conclusion, the local methane production could be technically substituted by non-fossil CO_2 , but with hitherto unknown costs.

For a future outlook of the product demands and production rates, no reliable data was available. However, trends indicate an increased consumption in the near term [80,86]. A study commissioned by the German Federal Ministry of Transport [80,87] give a range of 1275 to 1688 PJ energy demand for fuels in road transport (excluding electrified vehicles), depending on the scenario for the development of vehicle electrification. This corresponds to 26.6–39.2 Mt of diesel fuel.

5. Conclusions

This paper has shown that CO_2 from non-fossil sources is a source of carbon that will continue to be available in the future. On the one hand, it functions as a resource, while on the other, it (temporally, with the option of a constant loop) reduces CO_2 emissions into the atmosphere. So far, only a minority of the globally available CO_2 is used for synthetic conversion into other commodities, despite the technical feasibility of so doing (see chapter 3.2). This indicates what will most likely be a barrier due to economic, political or acceptance reasons. Here, further research must be conducted to identify the specific reasons for hindrances and to develop counter measures. Additionally, more efforts must be made to promote the substitution of fossil-based carbon with non-fossil carbon, e.g. by biochemical conversion or cement production, as indicated in this paper.

This study highlights the limits but also the chances of biomass-respective non-fossil ${\rm CO_2}$ as future carbon sources. It focuses on high volume products with high turnovers (see Table 11). In a future work, products with lower turnover but much higher value could also be

^{**} Including taxes.

chosen as possible products to be derived from CO_2 . While these products often lack reliable data, they show higher economic performance due to the much higher product value, which favors low capacity production and thus could be more suitable for non-fossil CO_2 utilization.

Additionally, we suggest further research in the field of CO_2 scenarios and technology assessment. The applied scenarios offer only a rough overview of future development. Even more valuable would be scenarios based on agent base market modelling regarding the energy and product consumption markets and the involvement of experts with regard to future trends and policy development. Furthermore, research in the field of technology assessment can be intensified to make more solid assessments of the future viability of technologies in early stages of development.

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