



PREFERRED TECHNOLOGY OPTIONS FOR DAC AND BECCS SCHEMES BASED ON RESULTS OF ASSESSMENT

M-P2.2.





Figure 1: Schematic of a possible circular carbon economy, which is the basis for this report.



HELMHOLTZ-CENTERS AND AUTHORSINTRODUCTION





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EXECUTIVE SUMMARY

Bioenergy with Carbon Capture and Storage

Bioenergy produces half of Germany's renewable power today. To produce heat, electrical power and energy carriers from biomass, conversion processes are applied during which carbon dioxide (CO₂) is emitted. This CO₂ can be recovered by bioenergy carbon capture and storage processes (BECCS), consequently leading to negative emissions because CO₂ is removed from the carbon cycle. Thus, BECCS can deliver both energy and negative emissions. Heat and electrical power production from biomass is well established e.g. by biogas plants or combined heat and power plants. Also, CO₂ recovery from effluent gas streams is mature technology, therefore BECCS based on these technologies could be realized on relatively short term. Technologies to produce energy carriers from biomass such as synthetic fuels or biocoal are not yet commercially applied, but they are well developed and could be implemented relatively soon. In this report, eight BECCS technology options have been identified which appear as relevant and applicable for possible BECCS scenarios in Germany. These technologies cover a broad range of conversion scale, possible biomass feedstocks and CO₂ recovery potential. All technologies have a high technology readiness level (TRL) and feedstocks as well as products produced are compatible with the German energy system. For all processes, a technology description was elaborated on the basis of which mass and energy flows could be determined to assess the process efficiencies with and without BECCS and its CO₂ recovery potential.

Anaerobic digestion

Firstly, a biogas production process was considered by the classical heat and power application (CHP). For anaerobic digestion, a mix of bio-waste, manure and purpose grown crops was utilized as feedstock. The biogas produced, containing around 60 % of methane, is combusted in a 500 kWhel gas engine at 40 % electrical efficiency. For CO₂ capture, a post-combustion chemical absorption process is applied. In a second biogas application, the raw biogas is cleaned and upgraded for injection into the public natural gas grid by a larger plant of 1 MWth biogas production capacity. Separation of CO_2 is first conducted by water scrubbing at elevated pressure, after which raw SNG is further cleaned in an absorption column. Both biogas technologies are of TRL 9.

Biomass combustion

For biomass combustion a power plant of 500 MWel with a supercritical steam cycle was assumed, re-designedfrom formerly operation with hard coal. Wood biomass is used as feedstock. CO_2 is captured in a commercially available post-combustion amine-based absorption process. The around 10 vol.% CO_2 content in the flue gas are recovered by around 90%. Caused by the additional energy consume to facilitate CO_2 recovery, the thermal efficiency of the power plant was estimated to drop from 40% to around 33%.

Biomass gasification

For synthetic fuel production via gasification, three process variants have been considered. In the "classical" Biomass-to-liquids process synthetic hydrocarbon fuels are produced from synthesis gas via the well-known Fischer-Tropsch process. Synthesis gas mainly consists of carbon monoxide and hydrogen (CO, H2). For its production, woody biomass is gasified in a gasifier combined to a combustor in which the heat for gasification is generated and transferred to the gasifier by a solid heat carrier (dual bed gasification). The thermal fuel capacity was set to 200 MWth. CO₂ is obtained from two process streams: from the synthesis gas stream after water-gas-shift reaction by which the desired CO/H₂ ratio is adjusted on cost of CO₂ formation, and from the flue gas stream of the combustor. Roughly, one third of the feedstock carbon can be recovered by synthetic fuel production. In the second variant, CO₂ emissions during processing are omitted by addition of renewable hydrogen to the gasification process (PBtL). In this case, the feedstock carbon is retained nearly completely in the hydrocarbon product, but requiring substantial electrical power to produce renewable hydrogen by water electrolysis. The third technology option based on gasification aims at the production of hydrogen from biomass. Since biomass is a material low in hydrogen, this process may only become attractive when CCS creates added value. In this case, practically all

feedstock carbon can be recovered from the process in form of CO_2 , leading to correspondingly high negative emissions.

Biomass pyrolysis

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Biocoal may be an alternative carbon form for long term sequestration. For its production two types of pyrolysis processes each of 100 MWth capacity were considered. Slow pyrolysis up to 70% of carbon is recovered in the solid product, while the rest is released as CO₂, CO and some other gases. Although biocoal may be used as carbon material or energy carrier, it is considered for long-term soil applications due to its relatively high stability when produced at temperatures above 500 °C. At the same temperature, fast pyrolysis may be applied. Here, the finely grinded biomass is heated rapidly by a solid heat carrier, reacted within a few seconds after which instant cooling leads to a around 60 wt.% of liquid condensate. This biooil can be used as heating oil or may be upgraded to fuels by hydrotreating. Around 20 wt.% of the feedstock remains as biocoal including the minerals content of the original biomass. Volatile carbon compounds from slow and fast pyrolysis are combusted to produce the heat required for pyrolysis, after which all remaining carbon can be recovered as CO₂.

BECCS is an option for relatively soon implementation. For this purpose, many and/or high-capacity carbon capture plants needs to be installed and operated within the next ten to twenty years along with the infrastructure for CO_2 transportation and storage. In the carbon dioxide removal scenarios raised and evaluated within Hi-CAM the most useful technologies and process constellations can be investigated based on this work in view to their possible bioenergy provision and CO_2 recovery potential.

Direct Air Capture

Processes called Direct Air Capture, or short DAC, are technological solutions to filter CO_2 from the atmosphere. The systems use specific chemical interactions of the CO_2 with special materials to bind it and therefore remove the greenhouse gas from the air. DAC-processes generally function as a two-step process: capture and regeneration. While captured, air is moved along the specialized material, called sorbent.

This sorbent can be either a strong alkaline solution or a solid. Solely the CO_2 reacts with the sorbent and forms covalent bonds, while most other components of the air are inert to the sorbent. To release the CO_2 the sorbent is heated. There are two different designs: The Low Temperature (LT)-DAC uses solid amine sorbents, which are regenerated using steam at around 100°C. High Temperature (HT)-DAC uses an alkaline solution, which must be regenerated at 900°C

The LT-DAC and HT-DAC solution are both suitable for a larger scale implementation. The decentralized approach favours the LT-DAC-system, because it has some benefits. At first, the HT-DAC is not scalable enough to fit into a HVAC or ventilation system. The classical chemical process is meant to exist on larger scales. Additionally, HT-DAC requires the handling of hazardous chemicals, which is not the case for LT-DAC, hence it is a lot easier to automate. Additionally, the low pressure drop eases the installation in existing ventilation systems, without compromising the function of the existing fans. With the addition of LT-DAC in HVAC systems a scheme without compromises for the end consumer could be build, which is the main goal of the project. Other technologies lack the easiness or readiness to provide such a system. Therefore, the choice is probably on LT-DAC-solutions. It should be mentioned, that the Electro Swing Adsorption is a viable contender as well, with similar benefits like the LT solution but is still in a very early stage of development, so predictions are difficult.

Syngas Production

The production of syngas using CO₂ from DAC has been modelled and assessed for Solar TCC, PEM + rWGS and SOEC pathways. Additionally, three different H2:CO ratios have been analyzed for each of pathway. Results do not show relevant differences between the hydrogen to carbon monoxide ratios regardless of the chosen pathway. Nevertheless, two clear tendencies can be observed when comparing pathways: PEM + rWGS and SOEC strongly rely on electricity, while the energy input for the solar thermal approach is mostly heat. Although the total energy demand is lower for the electrolytical pathways, Solar TCC might be more efficient when considering the intrinsic energy losses of electricity production. However, the solar approach might not be feasible in certain geographical locations with poor solar

radiation and its performance is still subjected to the sunlight intermittency. Last but not least, models forecast that LT-DAC should provide enough water from the air moisture to feed the process in all the scenarios.

Energy supply

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One major obstacle for decentralized DAC and conversion plants is the supply with renewable energy. Synergies lower the power demand, e.g. by dual-use of the installed fans, so unused surfaces equipped with photovoltaics (so called Building integrated Photovoltaics) could provide the electricity. The substantially higher heat demand could be met at least partially by CSP. If the energy is produced locally, storage solutions must be implemented to cope with diurnal and seasonal variations in energy generation. An integration into the energy grid enables a constant capture operation. The decentralised plants, especially the energy intensive water splitting step, could serve as dynamic energy sink to utilize excess renewable power. If hydrocarbons are produced, they could be used as energy storage and converted back into energy for the grid. Such small scale building integrated capture and conversion plants could stabilize the grid, while occupying otherwise unused space and utilizing synergies to increase the efficiency.

Fuel synthesis

OThe production of different fuels from syngas was compared, namely methane, methanol and Fischer-Tropsch product. On the one hand, the models indicated that methanol synthesis is the pathway that generates lowest waste heat and shows the best yield per mol of syngas, but it also requires the highest electricity inputs per mol for compression purposes. In addition, its energy content (HHV) is considerably inferior, which explains the lower energy demand per mass of final product. On the other hand, Fischer-Tropsch is the only process that produces more electricity than it consumes, even though an oxygen input is required for the reforming of the hydrocarbon fraction below C5. While it can be safely stated that methanol and FT synthesis outputs are easier to store and transport due to higher energy densities, methanation should not be dismissed since it can be a valuable option given the already available natural gas infrastructure.

Electrochemical conversion

The direct electrochemical conversion of CO, into usable products has a high potential of being the goto solution for the far future. These systems (CO₂E) can convert the gas directly into the products without the need of several reaction and purification steps. Such a plant, which operates at near-ambient conditions could decrease the required complexity of a decentralized system. CO₂E could also be readily scalable and offer efficiencies potentially comparable to the classical approaches. The technology is currently at an early stage of development and therefore all predictions are based on current state-of-the-art and theoretical assumptions. The current high cost of the products is driven by investment and energy cost. In the future especially the investment cost could drop significantly, so that the electrochemical production of higher alcohols and acids could become more profitable than the synthetic fuel production routes currently available. The CO₂E scheme is therefore an approach, which should be closely observed but cannot be implemented at the present day.

Enhancing the fuel production by use of membrane reactors

A generalized membrane reactor model was developed in Aspen Custom Modeler and employed for the thermocatalytic conversion of CO_2 to methanol as an illustration. The impact of the membrane reactor employment on the reaction conversion and selectivity was demonstrated. We showed that membrane reactors are more impactful when the heat transfer mode is non-adiabatic. Later, the model was imported into the Aspen Hysys flowsheet and used within the overall methanol synthesis process. According to the simulation, a 35% power reduction and a 10% thermal exergy saving can be achieved for the conversion process under the best-case scenario (Ideally waterpermeable zeolite-based membrane, isothermal condition and 7500 kPa).



Outlook

This report represents a collection of technologies for a circular carbon economy based on expert views of the Helmholtz-Centers participating in the Helmholtz Climate Initiative. From here, the need for further research emerges clearly. On one hand the basic research on new materials for different applications, like membranes or catalysts, should be continued, while on the other hand technological development should be increased.

Especially the technologies with a low TRL, foremost the decentralized DAC process, need to be developed in detail to hit the market. Other from this technological R&D need, the preselection in this report should serve as a basis for the development of detailed scenarios, in which boundary conditions, e.g. building size, location, area etc., are well defined and a definitive selection of the best process is possible. Such scenarios could serve as a blueprint for real projects or lead the direction of political decisions.



Figure 2: Comparison of the efficiency and energy consumption per t of CO₂ for different simulated product synthesis with a low detail level.



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ABBREVIATIONS

Abbreviation	Meaning
AEL	Alkaline Electrolysis
BECCS	Bioenergy with Carbon Capture and Storage
BiPV	Building integrated PV
CDR	Carbon Dioxide Removal
CO2E	Electrochemical CO2-conversion
CSP	Concentrated Solar Power
DAC	Direct Air Capture
DNI	Direct Normal Irradiation
ESA	Electro-Swing Adsorption
FTS	Fischer-Tropsch-Synthesis
нни	Higher Heating Value
HI-CAM	Helmholtz Initiative- Climate Adaptation and Mitigation
HT-DAC	High Temperature- DAC
HTF	Heat Transfer Fluid
HVAC	Heating, Ventilation and Air Conditioning
LT-DAC	Low Temperature- DAC
MENA	Middle East and Africa
PEM	Proton Exchange Membrane electrolysis
PtL/P2L	Power-to-Liquid
PtX/P2X	Power-to-X
PV	Photovoltaics
rWGS	reverse Water-Gas-Shift
SOEC	Solid Oxide Electrolysis Cell
ST	Solarthermal
TCC	Thermochemical Cycles
AEL	Alkaline Electrolysis



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INTRODUCTION

The IPCC special report (Rogelj et al. 2018) issued 2018 illustrates that global warming until the end of century of 1.5°C, compared to preindustrial levels, already bears considerable risks for humans and life on Earth. The report shows, that this goal, which is half a degree less than stated in the Paris Agreement, is feasible, if greenhouse gas emissions are brought to zero until mid-century followed by substantial CO2 removal.

Against this background, the Helmholtz Association offers a wide range of expertise in the various research fields which it wants to combine within the HI-CAM platform in order to generate knowledge and increase the visibility and impact of its numerous climate related research activities. Furthermore, it aims to strengthen the science-policy interface in this important field through an intensified stakeholder dialogue at all scales, from local to regional, national and European level. Last but not least, HI-CAM will promote inter- and transdisciplinary research and support young scientists in the development of their careers in this societally important research area.

The project consists of two main parts, so called Clusters: In Cluster I, called Mitigation, possibilities to reduce greenhouse gas emissions and limit global warming are assessed. Cluster II, adaptation, researches measures to deal with the consequences of global warming.

The mitigation part, in which horizon this report lies, aims to evaluate and pave the way for possible routes to reach Net-Zero and thereby also to provide scientifically sound and transparent information on the potential of key technologies under different scenarios as well as against the background of the specific economical and societal feasibility. A major part of the mitigation options is the circular carbon approach. This is a concept, where no carbon is gained from fossil reserves, but instead is obtained in form of CO2 directly from the air or from recycled products, like plastics. (Compare Figure 1). This approach enables the production of carbon-based products, such as hydrocarbon fuels or polymers, without generating net positive greenhouse gas emissions. This report focuses on the large cycle with gaining CO2 from the air and using this to generate products or negative emissions. For the capture of CO2 from the atmosphere, there are two possibilities. The first is utilizing plants, that convert the gas into solid biomass by photosynthesis, which is then harvested and further converted into energy and pure CO2 in a process called bioenergy with carbon capture and storage (BECCS), described more detailed in chapter 1. The second option is Direct Air Capture (DAC), which along with the subsequently following technologies to convert the CO2 into energy carriers is described in the following Chapters 2 to 7. This technological solution filters the CO2 from the air and provides it to conversion schemes, which turn it into useful products.

This report gives a collection of feasible technological options to create such a closed carbon loop, where no additional CO2 is added to atmosphere, while providing the still necessary carbon containing products needed by society. It should be stated, that this report is no complete systematic assessment of every available option, nor is the aim to choose one best technology. It shows a variety of technological options, which are selected by the experts of the contributing Helmholtz-Centers and could fit well in a circular carbon economy. This report should serve as a bases for scenario development and detailed technoeconomic assessments and show the relevant deciding factors, not to make this decision.

1 BIOENERGY WITH CARBON CAPTURE AND STORAGE

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Bioenergy still contributes by more than half to the share of 16.6 % renewable energies in the today's Germany primary energy carrier mix. Mostly solid biofuels are used to produce heat for domestic heating (45%), industry (16%), commerce, trade, and services (12%) (85.5 % of 179,9 TWh renewable heat). Heat provided by Biogas makes around 9% out of 201 TWh renewable power. Bioenergy provided by around 21% (50.4 TWh) from combined heat and power plants mostly from biogas (58%) but also from solid fuel (21%) combustion. With 44.1 TWh biofuels contribute 5% to the transportation fuel demand. In total, this makes 1 PJ bioenergy within 11.76 PJ primary energy demand in 2020 (FNR 2020, 2021). To produce heat and energy carriers from biomass, conversion processes are applied during which CO2 is emitted to different extent. To avoid its emission this CO2 can be separated by carbon capture processes from the various gas streams for subsequent storage or utilization (CCS/CCU) of the so recovered greenhouse gas. The combination of bioenergy with CCS is thus called BECCS (bioenergy with carbon capture and storage), essentially leading to negative emissions because CO2 is permanently removed from the carbon cycle by that way. As other carbon dioxide removal (CDR) technologies, too, BECCS still is subjected to great uncertainties in terms of realistic potentials, possible environmental impacts, additional costs and on its further implementation and socio-economic effects. For the future bioenergy use, however, CO2 extraction by BECCS may become decisive role, because a BECCS plant can delivers two products: energy and negative emissions. According to a given time and scenario, there may be a demand to prefer one product over the other one. The achievable span between both products for a specific technology depends significantly on the type of process and type of bioenergy. This trade-off is investigated in the HI-CAM project as part of the overall technology assessment on carbon dioxide removal options (Project 1, WP1.1.2). In this report, technologies are identified, which are expected to be continued or may become relevant for bioenergy production in the next decades in Germany.

During biomass processing for the production of chemical energy carriers or heat/power CO2, emissions arise which can be captured for storage or for chemical conversion. For this purpose, it can be re-used on site of the BECCS plant via addition of hydrogen from renewable energy powered electrolysis. Alternatively, biomass can be converted into biochar for long-term soil applications, e.g. by pyrolysis processes. In the Academies project "Biomasse im Spannungsfeld zwischen Energie- und Klimapolitik" led by UFZ, a number of bioenergy providing processes have already been identified and investigated in regard to their principal suitability and potential for CO2 removal (Klepper 2019). The range of processes has now been extended within the HI-CAM project by additional technological pathways, which are considered to be relevant to the German energy system. These processes were modelled based on practical data from already existing commercial or from pilot plants of sufficiently high technology readiness level TRL > 6 in order to determine the mass and energy flows. From this work, it will be possible to carve out the possible trade-off between bioenergy production and CO2 emission reduction potential, which was elaborated quantitatively for different types of biomass, conversion technologies and carbon storage forms relevant for Germany. Criteria such as the CO2 separation degree and mass potential of a certain process, its technology and market readiness level, efforts to be spent for its implementation in terms of energy and costs were be quantified and evaluated for its application potential in Germany within this project. On this basis, a more elaborated and extended tool is beeing be developed allowing for early stage evaluation of the BECCS potential within different scenarios in close cooperation with Project 1. This report presents and describes the technologies considered for the BECCS options along with the selection criteria applied.



1.1 Introduction

BECCS is considered as one of the most viable and cost-effective options to achieve negative emissions (Babin et al. 2021). It has gained a large importance in climate scenario pathways presented by the Intergovernmental Panel on Climate Change (Rogelj et al. 2018) to limit global warming to 1.5 °C, as indicated in the Paris Agreement (UNFCCC 2015). BECCS is not a one-technology concept; it refers to a wide portfolio of technological options, which follow the principles as depicted in Figure 3. They convert biomass into energy, capture CO2 released in this process and store it under the ground or in long-lived products. Alternatively, biomass can be converted into biochar, which can be stored e.g. in soil applications or as long living materials (left part in Figure 3). In this case, bioenergy may be generated to cover the process energy demand, but not for export as bioenergy. Given that plants draw CO2 from the air as they grow, energy generated from biomass provides a neutral to negative carbon balance (IEAGHG 2011; Kemper 2015). Most of the processes may be tuned in a way to maximize either the yield of bioenergy or that of captured carbon. In case that a solid carbon product is obtained this can either be used energetically or directly stored e.g. in soil applications. The variety of possible BECCS processes may be divided into four main sections related to biomass feedstock supply, conversion process, carbon capture, and carbon storage.

Diverse types of biomass can be used in BECCS processes:

- First-generation energy crops (sugar or vegetable oil providing plants like e.g. maize, sugar beet, rape seed),
- Purpose grown lignocellulosic biomass: lignocellulosic perennial crops like miscanthus or short rotation coppices),
- Forestry and agricultural bio-products and residues, mostly lignocellulosic material like straw wood thinning,
- Other bio-residues and -waste like, e.g., green waste from parks and gardens, roadside and track clearance, organic municipal solid waste (bio-MSW)),
- Macro- and micro-algae.

Due to sustainability concerns related to a.o. land use change, impacts on biodiversity and water consumption, especially the last three categories of biomass seem to have the greatest potential for the future.

All-in-all, biomass residues and sustainably grown bioenergy plants provide substantial potential. Today between 66 % and 84 % of biogenic residues are already in use, leaving a potential of 14-48 Mt (dry matter) to be mobilized for other applications in Germany (Brosowski et al. 2019). From the agricultural area cultivated in Germany, around 20% are occupied by energy plants mainly for biogas, biodiesel and bioethanol production providing additional potential (FNR 2020).

Biomass can be converted into bioenergy in the form of heat, electricity, or solid, liquid and gaseous biofuels in different ways: by thermal processes (combustion, gasification, pyrolysis), fermentation, anaerobic digestion, or chemical reactions (e.g. hydrogenation, esterification). While the bioenergy production process of BECCS is in most cases a mature technology, the carbon capture and storage (CCS) part is currently being developed in demonstration and pilot projects around the world (Consoli 2019; IEAGHG 2020; Global CCS Institute 2021).





Figure 3: Bioenergy carbon use, capture and storage options

Up to date 10 out of 13 completed or operating BECCS projects involve ethanol plants (in the US, Canada, the Netherlands, Sweden, Belgium and the UK) with remaining 3 projects involving a waste incineration plant (Saga City, Japan), a pulp mill (Saint-Felicien, Canada) and a power generation plant (Mikawa Plant, Omuta City, Japan). Another 10 projects are in development (in Norway, the UK, France, Sweden, the US and Brazil) and 5 have been cancelled (in the UK, the US, Tanzania, Germany). In Germany one pilot scale site for CO2 storage (for various capture sources) in Ketzin has been developed and operated over a period of 13 years (2004-2017). CO2 injection into an underground storage has been performed from 2008 to 2013, followed by a post-injection phase. A total of 613 t of CO2 (mixed with 32 t of N2) were injected, and the overall project demonstrated the feasibility of saline aquifer CO2 storage and applicability of geophysical methods for monitoring (Lüth et al. 2020).

Recent results of a study (Fajardy et al. 2021) show that global economic costs and the carbon prices needed to meet the stabilization targets for a 1.5 to 2 °C scenario in the second half of this century are substantially lower with technology already available. That way, BECCS acts as a true backstop technology at carbon prices around \$240 per ton of CO2.

Interestingly, in another recent study in UK it turned out that is was more cost-effective to deploy all three technologies investigated there (Biomass combustion with CCS, Biomass-CHP-CCS, and biohydrogen production with CCS) in combination rather than individually (Bui et al. 2021).

On a global scale there are around 59 EJ of bioenergy used worldwide. Close to 90% is contributed by solid biofuels, mainly fuel wood, charcoal and black liquor. Liquid and gaseous biofuels add around 6% each (Thrän et al. 2018). In order to build up the necessary capacities, the large-scale implementation of BECCS in many climate scenarios starts already between 2020 and 2030. The use of bioenergy amounts to a total of up to 400 EJ in these scenarios, but which is a factor of 2 – 4 larger than the lowest estimates of a sustainably usable bioenergy potential (National Academies Press (US) 2018). This could lead to significant trade-offs with the



preservation of ecosystems and biodiversity as well as ensuring food security, if not agricultural yields can be increased significantly or a more plant-based diet is introduced to reduce areal demand for food production. However, in many those climate protection scenarios, BECCS is considered as the only CDR technology until now. This underlines the importance to include other technologies as done in the HI-CAM project. At the end, it will be a mix of different technologies to meet the overall demand for CO2 removal. (Bauer et al. 2018) The waiver of BECCS would do not necessarily lead to a decrease in the need for bioenergy. Some climate protection scenarios based on BECCS renounce a similarly of even higher bioenergy use than scenarios with BECCS. (Bauer et al. 2018) The employment of others CDR technologies, however, could reduce the need for BECCS and also lower the bioenergy utilization. Therefore, the interrelation of sustainable use of bioenergy potentials, environmental impacts and food competition may be investigated independent of the employment of CCS].

1.2 BECCS Technologies

In principle, there are five bioenergy technology options with relatively high technology readiness levels, which may be utilized for BECCS on short term. Also, a variety of carbon capture technologies are available, the applicability of which depends on the gas volumes to be treated and the herein CO2 concentrations. Some basic information is compiled in Table 1. In the above-mentioned Academies project, the number of exemplary technology pathways was limited to biogas plants to produce methane for injection into the gas grid, combined heat and power plants with CO2 capture, and a biorefinery concept for synthetic fuel production based on syngas production. The latter could be operated in energy autarkic mode with limited incomplete carbon. In all these processes CO2 is available from gas streams with a substantial CO2-content of 15-50 vol.%. Especially in oxyfuel combustion with pure oxygen or oxygen-enriched air, the flue gas shows ahigh CO2 content enabling efficient capture. In the HI-CAM project a broader range of technologies was considered, from which a selection was chosen based on criteria relevant for their application potential in Germany. In most processes, CO2 is the carbon compound for separation and sequestration. However, pyrolysis allows for the production of biocoal as the main (slow pyrolysis) or by-product (fast pyrolysis) for chemical and energy applications, but also for long term storage in soil applications.

Type of conversion plant	TRL	Plant size	CO2 concentration range
Combustion with air	High	Small	CO2, 15-20 %
Combustion with oxygen	Medium	Large	CO2, > 90 %
Biochemical plant	High	Medium	CO2, < 50 %
Gasification plant	Medium	Large	CO2, > 20 %
Pyrolysis plant	High	medium	Biochar

Table 1: BECCS options within bioenergy production processes.

Methane pyrolysis is an emerging technology of some interest, but which is not included in this work due to its early stage of development (Sánchez Bastardo et al. 2020). All these the principally suitable technologies are described in the following. In the next chapters, the methodological approach is explained to identify those BECCS pathways which have been selected for further evaluation.



From combustion and fermentation gases, about 90% can be removed in an absorption-desorption cycle with liquid solvents. In self-sustained gasification processes with downstream synthesis, 1/3 up to half of the carbon contained in the biomass can be converted into carbon containing products, correspondingly around 1/3 of the carbon input can be recovered. After a moderate purification, CO2 can be liquefied by compression and transported in a pipeline, by a truck or a ship to a safe storage site: either an empty oil or gas cavern, a selected underground aquifer or the deep ocean.

Char yields from either conventional charcoal production (C-yield ca.75 %), torrefaction (C-yield ca. 85 %) or fast pyrolysis (C-yield ca.25 %) are different. Biochar can be stored in engineered sites or used as a constituent of "terra preta" (like soil). This is a mixture of char, soil and manure, which was used by the American Indians as a highly fertile soil for efficient crop cultivation. Porous bio-chars in soils are very stable, store water, and can survive centuries if the production temperatures are sufficiently high. For nutrients contained or added, biocoal acts as an ion-exchanger with potential to improve soil quality and fertility. A potential disadvantage can be an albedo reduction by large black cropland areas, which might contribute to global warming potential

1.2.1 Biochemical conversion

A variety of energy carriers and organic, chemical products can be produced by fermentation. Major products today are bioethanol (around 80 Mt/a) and the amino acid lysine (1.5 Mt/a); other chemical products are organic acids like acetic, lactic acid, succinic or citric acid, other alcohols like butanol, hydroxymethyl furfural and hydroxyalkanoates. Among the gaseous products biomethane (biogas, SNG (substitute natural gas)) is the most prominent, commercially established product. New fermentation processes, which allow an easier product separation from the fermentation broth are under development, e.g. isobutene is removed as a gas (Mitrovich und Wichmann 2017), or farnesene, which separates in an upper liquid phase and is intended to be used as diesel fuel component. Mostly sugar and starch are the basis for commercially established processes so far.

Operator	Location Feedstock		Ethanol production capacity (m ³ /year)
CropEnergies Bioethanol	Zeitz, Sachsen-	mainly wheat (possible also	360.000
GmbH	Anhalt	other grain types)	(315.000 t/y)
VERBIO Schwedt GmbH	Schwedt,	rve triticale com	230.000
VERDIO OCHWCat OHIDH	Brandenburg		(200 t/y)
Nordzucker AG Klein Wanzleben	Wanzleben-Börde, Sachsen-Anhalt	sugar beets (raw juice, thick juice, molasses)	130.000 (100.000t/y)
VERBIO Zörbig GmbH	Zörbig, Sachsen- Anhalt	whole crop of different grain types	100.000 (60.000 t/y)
Consun Beet Company GmbH & Co. KG	Anklam, Mecklen- burg-Vorpommern	products of sugar beet processing	66.000
Sachsenmilch Leppersdorf GmbH	Leppersdorf, Sachsen	whey residue	8.000

Table 2: Bioethanol plants in Germany



Bioethanol allows for significant and easy CO2 separation due to the formation of two molecules of CO2 per each molecule of ethanol (C6H12O6 C2H5OH + 2 CO2). From the around 1.1 Mio.t of bioethanol consumed in Germany around 650 kt are produced domestically, the rest is imported mainly from European countries. According to the simplified reaction equation, the CO2 emissions of the here produced bioethanol is equivalent to around 1.2 Mio.t of CO2, which can be recovered as relatively clean gas. Parts of that bioethanol are used as fuel component for gasoline blends or to produce MTBE. Since the production of first generation biofuels utilizing purpose grown crops is limited by the Renewable Energy Directive (RED) to a maximum of 7%, an increase in bioethanol production is not expected. Around 760 kt of bioethanol were used in the transportation sector; most of it was imported from within Europe (Naumann et al. 2019). Other biotechnology pathways emitting significant amounts of CO2 appear as not relevant in Germany.

Increasing interest is devoted to the use of lignocellulosic biomass. Sugars contained in the cellulose and hemicellulose can be recovered by up to around 70% by different pulping processes. By-produced lignin, making up to 25% of the lignocellulosic material, may be used energetically or, in perspective, for the production of fuels and aromatic chemical products. In such a 2nd generation process, the first step is the production of a 15 wt.% aqueous sugar solution as an intermediate platform via acid or enzymatic hydrolysis of the cellulose and hemicellulose fraction of lignocellulose. In a second fermentation step or within an integrated process, microorganisms convert the carbohydrate containing solution selectively to ethanol or other organic compounds. By ethanol production, about one third of the carbon in the sugar is released as a relatively pure CO2 stream without separation costs and is used or stored after compression and pipeline transport.

After break-through to marketable technology was achieved around 10 years ago (see Table 3), several demonstrations, first-of-its-kind and commercially operated lignocellulosic bioethanol plants have been erected worldwide (see Table 3). However, due to a still difficult economic situation several of them had already been set on hold or even decommissioned (IEA Bioenergy 2021).

Company	Abengoa, partners (Trilantic since 2017)	β-Renewables, partners (Versalis since 2012)	Clariant
Location	Hugoton, KA, USA pilot Salamanca, Spain	Crescentino, Italy pilot Alessandria, Italy	Straubing, Germany
Development stage	First of its kind	First of its kind	pilot
Conversion capacity	350000 t/a	270000 t/a	4500 t/a
Ethanol output capacity	60000 m3/a	40000 t/a	1000 t/a
Lignin combustion	70 MW	13 MW _{el} , 39 MW _{th}	n.a.
Main biomass types	corn stover, wheat straw	rice and wheat straw, arundo donax, giant reed	cereal straw
Operation start year	2013	2013	2012
Process specifics	Fermentation and enzymatic hydrolysis	Simultaneous hydrolysis and fermentation	"one pot" $C_5 + C_6^-$ sugar fermentation

Table 3: Comparison of some break-through cellulosic ethanol projects



Anaerobic digestion (AD) is another biochemical process, in which a raw biogas is produced from biodegradable material in a decomposition process led by a bacteria consortium (acetic acid-forming and methane-forming bacteria) in the absence of oxygen. The most common types of feedstock used for biogas production are: energy crops, crop residues, animal manure, wastewater sludge, organic fractions of municipal solid waste (bio-MSW), food processing residues, and recently also algae. Before being fermented, the feedstock may require a pre-treatment (e.g. drying, crushing). The AD process is controlled by many factors, including temperature, pH-value, organic matter content, carbon/nitrogen ratio. The resulting biogas composition strongly depends on the used feedstock, however typically it consists of methane (45-75%), CO2 (25-55%) and low amounts of other chemicals (e.g. N2, O2, H2S, organic sulphur, NH3, siloxanes and water). Other by-products of biogas production are solid and liquid residues (digestate) which can be used, e.g. as a fertilizer (Paolini et al. 2018). Anaerobic digestion is a process which facilitates effective management of residues and allows biomass and nutrient cycling in a closed loop (Arthurson 2009). Thanks to its specifics, it can provide both base load power, as well as be a flexible option in systems based on solar and wind power (Lauer und Thrän 2018).

Germany is a leading biogas country in the world. There are around 10.000 biogas plants in Germany with an overall capacity of approximately 30.000 GWh/a of electricity and 18.000 GWh/a of heat production. Although biogas does not have the same specifications as a natural gas, it can be upgraded to biomethane in order to reach natural gas quality. This is achieved by separating the CO2 and most of the impurities from the raw-biogas. The resulting quality of biomethane is determined by the upgrading technology, usually reaching >96% of CH4 and <2% of CO2. Typically, 1-2% of CH4 losses and 95-96% of technical plant availability are reported (Xie 2020). Biogas can be upgraded in physical, chemical, physio-chemical and biological processes. There are several fully developed technologies available for CO2 removal, among which adsorption and membrane separation are the most commonly used ones, realized in around 200 of the biogas plants in Germany. After reaching adequate quality, biomethane can be injected into existing gas grid or be used in gas-powered transportation (in cars, buses, trains or ships).



1.2.2 Combustion

Combustion aims at the production of heat, releasing a maximum of energy in the hot flue gas, which is used for direct heating purposes or for power production via established steam cycle technologies. After biomass combustion and heat recovery, the CO2 can be separated from the cooled flue gas. According to the conversion scale and type of combustion process CO2 separation may be conducted by different processes such as absorption/desorption cycles or membrane processes, followed by compression and transfer to a storage site. Compared to fossil fuel fired boilers, biomass combustion efficiency is lower; CCS consumes therefore a higher percentage of the generated energy. In a self-sustained process, where energy supply is used for harvest, transport and operation of combustion and CCS facilities, only about half or even less of the generated energy remains for utilization.

Oxygen-enhanced combustion generates a low flue gas volume without or only little N2-dilution, after water condensation at ambient temperature essentially composed of only CO2 and small amounts of water vapor and O2 surplus. After drying, this flue gas can be compressed, liquefied and stored or used. This avoids an expensive CO2 capture step, but at the expense of additional oxygen production cost. That way oxyfuel combustion could benefit from increasing water electrolysis for hydrogen production, by-producing oxygen. To reduce the otherwise extremely high combustion temperature, the cooled off-gas must be recycled several times for dilution to the combustor. This oxyfuel technology is also attractive for the combustion of special wastes with low heating value, but not yet mature; RD&I efforts are still continuing (Allam et al.).

As solid fuel, mostly wood chips or pellets are used. The combustion characteristics of biogas depend on its composition. High CO2 ratio in biogas has a strong inhibitory effect on its combustion, and biogas combustion rate is slowed (Deng et al. 2020).

1.2.3 Gasification

Gasification means the conversion of lignocellulosic biomass into producer or synthesis gas, depending on its use either for heat and power or for synthetic fuels and chemicals production, respectively. For this purpose, a gasification agent needs to be added to facilitate the gasification reactions, typically air, oxygen and/or steam. In BIGCC plants (biomass integrated gasification combined cycle), biosyngas is usually produced by gasification with oxygen under pressure. Small gasification reactors may be heated externally (allothermal processing), while in larger scale reactors the heat required to facilitate the gasification reactions is achieved by partial oxidation consuming a certain share of the fuel by combustion. (autothermal processing). Main products of biomass gasification are CO, H2, CO2 and H2O (the amount depending on the process technology and design), little amounts of CH4 and impurities and contaminants, which need to be removed by downstream purification processes. For chemical use, the CO/H2 ratio needs to be adjusted by the water gas shift reaction (CO + H2O <=> H2 + CO2). Process integrated CO2 separation as conducted already today in the coal-to-liquids processes (CtL) leads to a pure pressurized CO2 stream, which is directly suited for recovery, use or disposal. In Table 4, a selection of pilot and demonstration plants with Technology Readiness Levels (TRL) between 6 and 8 for the conversion of lignocellulosic biomass into different types of synthetic fuels via gasification pathways are listed. Due to the importance of Scandinavian wood industries, the earliest efforts can be observed in this region. Many more examples of plants for synthesis gas based fuel production are given in the global database of biomass conversion facilities of IEA Bioenergy (IEA Bioenergy 2021), including advanced biofuels, combustion, gasification, and pyrolysis plants. The examples in the table provide evidence of the multitude of options to set up a process chain regarding feedstock, pretreatment, gasification and synthesis technology. The broad range of possible products from synthesis gas is presented in Chapter 5 in more detail.

Table 4: Selected pilot or demo projects for biomass to liquid (BtL) processes.

BtL Project	Feedstock	Key Technologies	Products
LTU Green Fuels, S	Black liquor,	Small	CO2, 10-20 %
pyrolysis oil	Chemrec process with EFG, 2 MW, 30 bar, 4 t/d pro- duction	DME, methanol	CO2, > 90 %
Güssing Renewable Energy Multifuel Gasifi- cation, A	Forest biomass and others	Repotec fast internally circu- lating fluidized bed (FICFB), 8 MW, atm. pressure	CHP, SNG (1 MW), FT plant (slip stream)
NSE Biofuels Oy, Var- kaus, S	Forest biomass	CFB, 12 MW Foster Wheeler, hot filtration, catalytic tar reforming, (5 MW for synfuel application)	Heat for a lime kiln, FT- products (slip stream)
bioliq®, KIT, D	Lignocellulose bio- slurries	Fast pyrolysis 2 MW + 5 MW entrained flow gasification, hot gas cleaning, 80 bar	MeOH/DME, gasoline
Goteborg Energie AB, GoBiGas, S	Forest biomass	metso/repotec Dual bed, 20 MW (50.000 t/y SNG)	Biomethane
Total, BioTfuel demo, F	Forest biomass	Torrefaction + Uhde Prenflow EF, 15 MW, 8000 t/d FT pro- duct	FT-products
Värmlandsmetanol, S	Forest biomass	Uhde-HTW gasifier, 111 MW	Methanol
Växjö Värnamo Biomass Gasification Centre, S	Forest biomass	Foster Wheeler pressurized CFB + hot gas filtering	Heat & power, clean syn- gas
Woodland Biomass Re- search Center, LLC Ther- mal Reformer Synthesis West BiofuelsWoodland, CA	Forest biomass	Dual fluidized bed gasifier, 5 t/d waste wood,	FT products
Red Rock Biofuels, Oregon, US	Forest biomass	Gasification, 44.0000 t/y FT liquids	FT products

In gasification, CO2 is produced due to partly combustion of the fuel in order to reach the high temperatures required for syngas production above 800 or even about 1000 °C, depending on the technology applied. This CO2 needs either to be recovered from the syngas, when autothermal gasification is applied, or from the dedicated combustion unit e.g. in the dual bed technology. Roughly, about one third of the initial biomass carbon can be captured as CO2 in this way, while, at best, the other carbon is converted to products.

Instead of emission or storage of the by-produced CO2 in gasification processes, this could be converted to syngas by the reverse water-gas-shift reaction by help of renewable hydrogen produced from water and renewable energy by electrolysis. This way, a combination of Biomass-to-liquids (BtL) and Power-to-Liquids (PtL) process would be attained. From an economic point of view there is some evidence that the combined process may be more competitive than the single BtL and PtL processes (Albrecht et al. 2017). This is due to the much



higher product yields, since essentially all bio-carbon is converted into organic products. Vice versa, also hydrogen could be produced from biomass by shifting all CO contained in the synthesis gas completely to CO2 and hydrogen via the catalytic conversion with water (Biomass-to-hydrogen). This is a most efficient route, since there are no exothermic reactions necessary like e.g. in the case of methanol, SNG, Dimethyl ether and hydrocarbon synthesis. Therefore, the production of hydrogen maintains the largest share of feedstock bioenergy.

In a future world without fossil fuels, the demand for thermochemical biomass gasification is determined by the demand for indispensable syngas products like organic chemicals, polymeric materials and liquid hydrocarbon fuels for aviation, heavy duty trucks and ships. A very rough, simplified estimate for the thermochemical as well as for the biochemical route assumes that about 1/3 of the biocarbon fraction is converted into the desired products. The carbon in the products is usually liberated as CO2 in the course of several years during or after use as a fuel, if not long-lasting materials are produced. Used carbon-based products are either collected and recycled or released as CO2 by combustion in municipal solid waste incineration plants or disposal and rot in the environment. Another 1/3 of the bio-carbon is used for energy for harvest, transport and CO2 disposal. The energy required for the BECCS variants 1-3 (Table 1) can, in principle, also be delivered by other renewable energies without principal differences in the technology. On the average only about 1/3 of the biocarbon will be available as CO2 by-produced in the bioenergy processes for capture and storage.

1.2.4 Pyrolysis

By biomass pyrolysis, solid char or biocoal, liquid condensates, and pyrolysis gases are produced, depending on temperature and residence time selected for the process (see Figure 4). Pyrolysis gases, often containing considerable amounts of CO, are usually combusted to supply the process energy. Today, biochar is used for various purposes: e. g. as charcoal for metal refining, barbecue, carbon reduction agent in chemistry, and as activated carbon. Tar constituents (vapors, which form a liquid phase after condensation at ambient temperature) form liquid condensates after cooling, also referred to as biooil or biocrude for energetic use. With regard of chemical use, pyrolysis tars have been used as raw material for the production of pitch, wood vinegar (acetic acid), wood spirit (methanol), acetone and numerous other organic chemicals. Wood tar – and later coal tar – was the basis of the first organic chemical industry. Today, mainly acetic acid is of main interest as a by-product.



Figure 4: Product yields for different types of pyrolysis processes characterized by reactor residence time and temperature

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Biocoal produced at elevated temperatures (typically > 500 °C) are considered persistent and stable storage product in soils. A mix of soil, manure and pulverized biochar is termed "terra preta" and has been used by the American Indians for centuries to improve soil fertility. Now it can be combined with biochar disposal, to remove carbon from the carbon cycle for several hundred years. A meta-analysis of char stability shows a small labile biocoal fraction of only ca. 3 wt.% with a short mean residence time of less than a year. The large recalcitrant fraction has a mean residence time in the soil of several hundred years (500 ± 400 a). Wood char with a low ash content produced at higher pyrolysis temperatures were found to be more stable than those with higher ash content (Antal und Grønli 2003). A comprehensive study of Umweltbundesamt in 2016 revealed the complexity of a potential use of biochar in soil applications (UBA 2016). Interactions with the soil water and nutrient content, soil and plant biology, effect on CO2 CH4 and NO2 emissions and relations to the fertilizer ordinance and other regulations need to be clarified. On a voluntary basis the European Biocoal Certificate was issued by the ITHAKA institute in Germany, providing guidelines to make sure that only biocoal with certain properties may be used in soil applications (Ithaka 2021).

Slow pyrolysis is also used for waste treatment, e.g. to recycle used tires, electronic scrap and other compound materials difficult for disposal. One example is the VTA Low Temperature Carbonization process making use of an indirectly heated rotary kiln reactor, which can flexibly be adjusted to the different types of feedstock. Pyrolysis of municipal solid waste in a rotary kiln, followed by final disposal of the pyrolysis products has been practiced commercially in Burgau, Germany, until 2016. The process was abandoned, because disposal of (combustion) products in Germany with more than 5 wt.% carbon is not allowed any more. Conventional charcoal production in piles and retort reactors at ca. 400 °C gives charcoal yields of 30-35 wt.%, which is around 70% of the theoretical yield. Very simple iron retort devices are used for barbeque coal production in small scale in many places in Germany. The only industrial plant available in Germany today is that of Profagus company, delivering different types of biocoal and also making use of the liquid products e.g. for acetic acid recovery or as boiler fuel. In Table 5 a selection of recent process developments to produce biocoal is compiled along with their process characteristics.

Manufacturer	Reactor type	Key parameters	Biomass input / biochar output
Pyreg P 1.500, D	Twin screw	500–700 °C, 12–30 min	2130, 530 t/a
Etia	Single screw	< 850 °C, 5-40 min	< 1500 t/a
Carbofex	Single screw	600-700 °C	500 / 700 t/a
Compag CPP1500	Fixed bed	< 450 °C	400-600 / 600 t/a
СТЅ	Moving bed (vertical)		990 / 330 t/a

Table 5: Selected pilot commercial plants for slow pyrolysis for biochar production. (does not include companies and plants already established e.g. for activated carbon production and other commercially established processes)

In Table 5 a selection of recent process developments to produce biocoal is compiled along with their process characteristics.

Fast pyrolysis produces a maximum of pyrolysis liquids (biooil), at a high 50-70 wt.% yield and some biochar and pyrolysis gas with both of 20 ± 5 wt.% each. Combustion of the pyrolysis gases can supply the process energy. Fast pyrolysis requires finely milled lignocellulosic material in form of dry, comminuted biomass particles with a characteristic length ≤ 1 mm. The particles are rapidly mixed in a few seconds at a temperature of 500 ± 30 °C with a ca.10-fold excess of a hot heat carrier, usually cheap and easy available sand.

Various reactor designs exist for fast pyrolysis, mainly utilizing fluid beds or mechanical agitation for the required instant mixing of heat carrier and fuel particles (Table 6). After rapid quenching, biooil is recovered containing several hundred chemical species. Commercially established is the use of this product for heat generation.

Table 6: Selected pilot or commercial plants for fast pyrolysis.

Manufacturer	Reactor type	Key parame- ters	Biomass input/biooil output
Envergent, RTPTM	Bubbling fluid bed	500 °C, sand heat carrier	
Fortum, metso, FIN	Circulating fluid bed	500 °C, sand heat carrier	50 kt biooil
Empyro, BTG, NL	Rotating cone	500 °C, sand heat carrier	20 kt biooil
KIT, bioliq®, D	Twin screw	500 °C, sand heat carrier	500 kg biomass

Advanced applications are the today investigated routes to use biooil for coprocessing in petro refineries (Van Dyk 2019) and for gasification. Here, the fast pyrolysis liquid and the biochar powder can be mixed to a pumpable, pasty bioslurry for gasification. There, the bioslurry can efficiently by converted in a pressurized entrained flow gasifier and gasified together with around 1/3 of the stoichiometric oxygen at \geq 1200 °C. The generated raw syngas can be either combusted in BIGCC plants or purified and catalytically converted to methanol, DME, hydrocarbon fuels and valuable organic products.



1.2.5 Carbon capture technologies

According to the operating principle, the main carbon capture technologies can be divided into three types of treatment: 1) pre-combustion capture, 2) oxy-fuel combustion capture, and 3) post-combustion capture. Each of those has its own advantages and technical issues. Pre-combustion capture technology means to gasify the fuel into clean to synthesis gas and to separate carbon dioxide before its combustion or other use and thus to avoid CO2 emissions. However, the concentration and pressure of carbon dioxide is increased, resulting in more convenient separation of carbon dioxide. Pre-combustion capture technology is the cheapest at present and already applied in fossil fuel gasification. The problem is that traditional power plants cannot easily apply this technology and a re-design is extremely expensive. New power plants may be erected, the construction of which is more costly than traditional power plants. Post- combustion capture can be directly applied to existing power plants. This CO2 capture route has relatively small, but still significant investments for its integration into the flue gas treatment train of a power plant. Carbon capture can be facilitated by chemical absorption, physical adsorption, membrane separation, and other approaches. Among them, chemical absorption seems to have the best market prospects for large scale conversion plants, but relatively high energy consumption and cost of equipment. For smaller scale like e.g. for upgrading of biogas to SNG for grid insertion, membrane technology is catching up as an alternative technology that is more energy efficient than chemical absorption with amines and may be scaled up to for larger plants. Oxy-fuel combustion capture combines the advantages of the other two technologies. It can not only be applied in conventional power plants, but also allows for CO2 recovery at beneficial high concentration and pressure. On the other hand, the cost of oxygen production needs to be added, so the oxyfuel combustion capture technology does not provide significant economic advantages so far (e.g.(Assen et al. 2016)).

It is generally assumed that post-combustion capture technology is the most feasible to be combined with combustion plants. The flue gas from combustion usually has the low partial pressure of CO2 and contains other gas components. Therefore, highly selective solvents are used for CO2 recovery, such as amine containing, that separate CO2 by chemical absorption. Monoethanolamine (MEA) as a solvent has extensively been studied and are established for recovery of CO2 in chemical processes. Other MEA-based amine mixtures used are diglycolamine (DGA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), and piperazine (PZ) (Deublein und Steinhauser 2008; Fredric Bauer et al. 2013). In addition, piperazine-based mixtures are also considered as CO2 scrubbing solvents. MDEA/PZ offers advantages over monoethanolamine (MEA) and MDEA alone because of its faster reaction with CO2 when compared to MEA or a blend of MEA and MDEA (Bishnoi und Rochelle 2002), by low regeneration energy consumption (Fredric Bauer et al. 2013) and resistance to thermal and oxidative degradation at typical absorption/stripping conditions (Closmann et al. 2009). Caustic solvents (sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide (Ca(OH)₂)) also provide the opportunity chemically to remove CO2 from the flue gas. Compared to MEA, NaOH has the advantage of being cheaper, more available and possessing a greater theoretical CO2 capture capacity (Yoo et al. 2013). Amino-acid salts (AAS) have a great potential for CO2 absorption. Some recent studies recommended AASs are potassium salts of taurine and glycine (Kumar et al. 2003; Vaidya et al. 2010), sarcosine (Knuutila et al. 2011), proline (van Holst et al. 2009), alanine (Park et al. 2014), serine, and I-aminobutyric acid (Song et al. 2012)



Table 7: Selected commercial CCS plants

Facility Name	CC technology	Adsorbent	Capacity	Location
Sleipner CO ₂ Storage	Post-combustion Oil and gas processing	Amine	2600t CO2/d	Norway
Snøhvit CO ₂ Storage	Post-combustion Oil and gas processing	Amine	0.7 million tCO2/y	Norway
Air Products Steam Methane Reformer	Pre-combustion Hydrogen Production		1 million tCO2/y	USA
Quest	Post-combustion Hydrogen Production	Amine	1 million tCO2/y	Canada

A schematic flow diagram of a CO2 adsorption process is shown in Figure 5. The CO2 containing gas stream is pressurized and directed into the absorber, where it flows upstream in counter current contact with the absorbent liquid (containing around 15 wt.%-30 wt.% MEA) from the top to remove carbon dioxide. The purified flue gas is recovered from the absorber top. The CO2 containing absorber solvent is pressurized and transferred to the stripper. In order to reduce the steam consumption during solvent regeneration, waste heat of regenerated lean amine solvent is used in an economizer to heat the CO2 loaded amine and cool down the lean amine. The CO2 rich amine enters from the upper part of the stripper. In the stripper CO2 is partly released from the solvent, which then enters the heater to further desorb CO2. The lean amine flows out from the bottom of the stripper before cooled in the heat exchanger and sent to the absorber again. The mixture of carbon dioxide and steam from the top of the stripper is condensed before sent to the knockout drum, from which the condensate water returns to the system, while carbon dioxide enters the subsequent compression process.

The first post-combustion capture pilot plant in Germany was developed, constructed and operated by RWE Power, BASF and Linde at the lignite-fired 1,000 MW Niederaussem power station in 2009. This project is aiming at an advanced optimized CO2-scrubbing technology for power plant application. 7.2 t of CO2 per day can be captured from a flue gas slipstream of the power plant downstream of the desulphurisationplant (FGD) moser (Moser et al. 2011b). The pilot plant was in operation with 30%-weight MEA,

(Moser et al. 2011a), the novel BASF solvents GUSTAV200 (Moser et al. 2011b) and amine-based capture technology OASE® blue (Moser et al. 2014).

Worldwide 64 CCS plants are operated commercially, of which 64 are located in America, 10 in Asia, and 13 in Europe. 11 new plants are expected to be operated before 2030 in Europe (Global CCS Institute 2020). In Table 7, some of the large-scale plants are compiled, making obvious that CO2 separation is technically feasible in small (biogas to SNG upgrading), but also in large scale.

Gas separation membrane technology is an alternative for the separation of CO2 from point sources in industry and energy generation. The employed membranes work according to the solution-diffusion principle, i.e. the membrane material is selected to allow CO2 to be dissolved more readily into the polymer than other flue gas components except for water vapor.





Figure 5: Schematic flow diagram of chemical CO₂ sorption



Figure 6: Two-stage membrane process for CO2 separation from flue gas

Once having been dissolved, CO2 diffuses through the polymer structure at a higher rate. In order for the principle to work, driving force has to be applied across the membrane. This driving force is the difference in chemical potential that can be realized as fugacity or partial pressure difference for gaseous systems. The membrane itself typically is of the flat sheet, thin film composite configuration, meaning that an approximately 70 nm thick CO2 selective separation layer is sandwiched in between less selective but highly permeable layers that in turn are deposited on a porous support structure. The most promising membrane materials are poly(ethylene oxide) containing block copolymers that exhibit a 60 times larger permeability for CO2 compared to N2 at ambient conditions. The flat sheet membranes are mounted into membrane modules of different geometries containing up to 150 m2 of membrane area. For post combustion CO2 capture, different process



designs have been tested and thoroughly investigated in different pilot scale and demonstration plants. In order to achieve high CO2 separation rates combined with high CO2 purities, two stage cascades have been designed. One such design is shown in Figure 6. Downstream of the not shown pretreatment (e.g. dust removal) the CO2 containing flue gas is fed to a blower delivering the gas at pressures of up 1.3 bar to the unit to be mixed with a recycle stream. The gas is cooled down in the Condenser 1 to remove water and superheated in the Heater to prevent condensation in downstream apparatuses. The Membrane Stage 1 separates the feed gas into permeate passing the membrane with a CO2 content of 60 to 70 mol% and a CO2 depleted retentate

stream. The driving force is generated by the vacuum pump operating at approximately 150 mbar on the permeate side. Downstream of the condensate removal in the Separator, the gas is compressed to 5 bar, cooled down in Condenser 2 and fed to Membrane Stage 2. In this stage, the permeate stream is enriched to a CO2 mole fraction exceeding 95 mol%. The retentate stream is led to a turbo expander for energy recovery and subsequently mixed with the feed stream of Membrane Stage 1.

1.3 Methodology for BECCS evaluation

The following approach has been developed to perform an early stage evaluation of BECCS technologies:

- Selection of BECCS technologies for an assessment:
 - a. Preparation of technology factsheets and development of model concepts of selected technologies
 - b. Data collection and quality control
 - c. Process simulations of selected technologies
- Feeding the collected data into the Technology Assessment Matrix (TAM) and application of traffic light system (Cluster IWP 1.1.2)
- Early stage assessment of BECCS feasibility in Germany

The subject of this report encompasses the first step of our approach. The selection of technologies as well as development and application of traffic light system for their evaluation has been built upon previous studies which proved a successful application of this method for an assessment of bioenergy technologies (Klepper und Thrän 2019; Thrän et al. 2020).

As criteria for technologies selection (see Chapter 1.4 for details) we were focusing either on state-of-the-art technologies (e.g. biogas with CHP, biogas upgrading for injection into the gas grid, biomass combustion for combined heat and power production CHP) or technologies on a lower readiness level, but being promising for development and application under specific German frame conditions. To put these technologies in a German context, exemplary model concepts were derived on the basis of individual plant concepts with clearly defined process configurations and technical parameters (Chapter 1.4).

In order to unify and systematize the data collected for these technologies, for each model concept a factsheet was established. To describe the technologies in a possibly comprehensive way, the factsheets include relevant data, a.o.: general technology data (e.g. type and scale of conversion, capture technology, feedstock, product, TRL), parameters of technical performance (e.g. net plant efficiency, CO2 emissions with and without capture unit), economic performance, location and infrastructure requirements. The data collection process has been conducted in parallel on each selected technology. Diverse data channels have been used including peer-reviewed literature, reports, as well as results of process simulations and researchers' assessment.

1.4 Technology selection for TAM evaluation

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From the above-introduced technologies, a selection was made in order to evaluate their potential for BECCS according to the criteria defined in the technology assessment matrix. For selection, the following criteria have been applied.

- Technology Readiness Level: The TRL should be high enough to allow for an evaluation based on representative data, if possible from practical operation of commercial plants. In case of pre-commercial technologies, at least pilot plant operation should have been achieved with TRL > 6.
- Feedstock relevance: As feedstock, types of biomass are utilized which are used and available in Germany. For biogas, a mix of manure, purpose-grown crops, and organic waste can be assumed. For combustion, gasification and pyrolysis wood was regarded as feedstock. However, also other types of the significant lignocellulosic feedstock potential in Germany may be taken into account. It is assumed that the share of bioenergy in the energy mix is not increased; however, change of use within the existing energy product variety may occur (e.g. domestic heat, vs. electrical power vs. gaseous and liquid fuels). In case of increasing bioenergy, production import of biomass needs to be considered.
- Product relevance: Bioenergy provides useful options for sector coupling, because either heat, electrical
 power and fuels can be produced. Therefore, several of these product options have been considered for
 evaluation. First generation biofuels were not regarded. Even though bioethanol from sugar and starch
 promises substantial CO2 recovery due to the formation of two molecules of CO2 for each molecule of
 ethanol. Biodiesel production from vegetable oil (mainly rapeseed in Germany) was found to be not relevant for BECCS. During production of vegetable oil and its conversion to methylester (RME) CO2 emissions
 appear as not significant.

In Table 8, the selected technologies are compiled together with some key data as contained in the above mentioned technical fact sheets. In the following sections, these are described in more detail.

1) assuming 40 vol.% CO2 in raw biogas and 8-15 vol. % in flue gas

1. Biogas CHP

There are several different ways in which biogas can act as a source of carbon for CCU/S systems. (Rodin 2020) distinguish between two main pathways, the first utilizing of CO2 captured from upgrading of biogas to biomethane, the second captures CO2 from combustion of biogas. For evaluaton, these two options have been selected and will be shortly described here.

Most of the biogas plants (approximately 90%; (DEA 2017)) use the produced biogas directly on site to generate energy in a form of heat and power in a cogeneration process (CHP) (Blockheizkraftwerk, BHKW). In this process biogas serves as fuel for an engine (e.g. gas engine, micro gas turbine, fuel cells) that drives a generator to produce electricity. Cogeneration uses the waste heat of the engine and the exhaust gas for heating or provision of hot water. A small part of the waste heat is usually used by the biogas plant itself, e.g. to keept the temperature in the digester constant. The efficiency of power generation with internal combustion engines ranges from 28 to 47% for electricity generation and from 34 to 55% for heat generation, depending on the size of the plant. Micro gas turbine systems have 26 to 33% of electric efficiency and 40 to 55% of thermal efficiency.

The highest electric efficiency of 40 to 60% can be achieved with fuel cell-based CHP units (FNR 2020). Direct combustion of biogas with air provides CO2 concentration in the range of 8-15%.



Technology	Product	TRL	Size / MW	CO ₂ concentration
Biogas CHP	Heat, electricity	9	500 kWel	45 – 50 %¹)
Biogas SNG	Substitute natural gas	8-9	1 MW	45 - 50 %
Combustion CHP	Heat, electricity	9	500 MW	10 – 15 %
Gasification for synfuel production	Fischer-Tropsch hydrocarbon fuel	6-8	100 MW	20 - 30 %
Gasification for hydro- gen production	Hydrogen	6	100 MW	< 5 %
Power assisted synfuel production	Fischer-Tropsch hydrocarbon fuel	< 6	100 MW	20 - 30 %
Fast pyrolysis	Bio-oil, bio-coal	9	100 MW	50 – 55 %
Slow pyrolysis	Bio-coal	9	50 MW	50 - 55 %

Table 8: Selected technologies and key data for BECCS evaluation

In our study anaerobic digestion was modelled as mesophilic digestion with an electricity consumption of 8% of the electricity produced, and a heat consumption calculated as the energy required to heat the substrates to 37°C (Tonini et al. 2016) and for solvent regeneration. As a feedstock we have been considering a mix of different types of bio-waste and residues (50%), manure (20%), and allowing up to 30% of purpose grown crops. The methane yield was estimated to be 60% of the theoretical yield. We assumed 1% fugitive CH4 losses from digesters. The produced biogas is combusted in an Otto engine with installed 500 kWhel capacity and an efficiency of 40%. The CO2 is captured in a post-combustion MEA-based chemical absorption process (chemical scrubbing). Because solvent regeneration uses heat from exhaust gas, the overall recovery of heat is reduced.

The generated electricity is fed into the public electricity grid, heat is fed into a local heating network and partially used on site. The CHP technology used to generate electricity from biogas is technically mature (TRL 9). However, up to date there are no commercially deployed biogas CHP installations with integrated CO2 capture for storage applications.

2. Biogas upgrading for biomethane production (SNG)

Biogas can also be used for production of biomethane and its injection to a gas grid. Before the injection, raw biogas needs to be treated to achieve natural gas quality and to comply with requirements stipulated in the relevant regulations (e.g. DVGW worksheets G280, G685). These include a.o. conformity with combustion parameters, maximal CO2, oxygen and water content in the upgraded biogas.

In our study we assumed the same conditions the for biogas generation process as described for biogas CHP option (same kind of feedstock and anaerobic digestion conditions), however, in this case we selected a bigger, 1 MWth plant. Separation of CO2 conducted by in a pressurized water scrubbing process. It is a process based on physical absorption which uses different solubility of gases (CO2, CH4 and H2S) in water.





Figure 7: Simplified scheme of biogas CHP with CO₂ capture.

Raw biogas is compressed before entering absorption column. Although CO2 loading capacity of water is lower than that of amine-based solutions and requires a larger quantity of scrubbing agent, the amount of water can be reduced by increasing the pressure. Furthermore, as H2S dissolves in water, it may avoid an additional cleaning step. The gas which leaves the column consists of 97-99 vol. % methane. Regeneration of loaded scrubbing water takes place through desorption with air. In addition, the resulting waste heat can be used on site, e.g. for the fermentation process. As biomethane processing is technically mature and commercially available technology, its TRL equals 9. For the grid injection raw SNG is pressurized, usually to 0.1-16 bar, depending on the type of transmission network (L or H gas grid) and an odorant is added. Other parameters (e.g. volume flow and Wobbe index) are monitored and adjusted by adding liquefied petroleum gas, if necessary (Fendt et al. 2016).



Figure 8: Simplified scheme of biogas upgrading to bio-methane with CO_2 capture.



3. Combustion CHP

To study biomass combustion for heat and power production (CHP) we have selected a 500 MWel power plant with a supercritical steam cycle, formerly run on hard coal. The conversion of coal-fired power plants to run on biomass may offer an opportunity to make an effective contribution to achieving the renewable energies targets (covering 65% of electricity demand by 2030 (BMWi 2020a, 2020b). Furthermore, supplying such plants with carbon capture units may provide a centralized source of CO2 for storage to address domestic emission targets. The conversion of coal plants into biomass plants has already been implemented in various locations in Europe, e.g. in Denmark (e.g. Studstrup CHP,(Ørsted 2016a, 2016b)) and Great Britain (Drax Power Plant (Drax 2021), Lynemouth Power (EP Power Europe 2021)).

We have selected a coastal location for our model plant which may help to cover water demand of the cooling system, as well as to provide access to low-cost biomass, if sufficient domestic feedstock supply would not be possible. We use both primary and secondary (waste-derived) lignocellulosic biomass. The flow of the processes in the plant is depicted on Figure 9. CO2 is captured in a post-combustion amine-based absorption process, which is currently commercially available benchmark technology (Pröll und Zerobin 2019). We assume >10% of CO2 content in the flue gas and 90% CO2 capture. The plant's thermal efficiency with CCS unit is lower than that of non-CCS bioenergy plants, as part of the waste heat covers the heat demand of CO2 capture system. In our study we estimate thermal efficiency to drop to 33%.



Figure 9: Simplified scheme of biomass combustion power plant with CO₂ capture unit (Pröll und Zerobin 2019).

4. Gasification for synthetic fuel production (BtL)

Three gasification scenarios with wood as feedstock were chosen. It is a relatively easy to gasify material and large pilot as well as commercial plants have been operated with this material. Therefore, a type of gasifier was selected which was specifically developed for biomass gasification and has proven long term operation and has a high TRL of 8. Based on the dual fluid bed technology, the schematic flowsheet is shown in Figure 10. In the dual bed technology, gasification and combustion for heat generation are carried out in two separated reactors, between which a solid heat carrier material is cycled in a loop. CO2 needs to be recovered from the gas streams of both reactors: from the synthesis gas stream after the water-gas-shift-reaction, and from the combustion reactor from the flue gas stream. Other types of biomass may be used as well for gasification, but may



require additional efforts specifically in case of ash-rich materials like straw or other grassy types of biomass. In this case, pre-treatment e.g. by leaching of soluble ash components or adapted gasification technologies need to be applied, like e.g. done in the bioliq-process for synthetic fuel production from ash rich feedstock. There, an entrained flow gasifier is used from which the ash is removed as a molten slag a high gasification temperatures >1200 °C. In perspective, entrained flow reactors may perform better in view of CO2 capture, because parts of the CO2 may recovered from a synthesis gas at higher concentration.

The dual bed gasification process was simulated based on a biomass cogeneration plant in Ulm. The process is shown in Figure 10. The dried biomass is fed to a dual fluidized bed for gasification. Olivin is used as a heat transfer medium to enable gasification reactions at 900 °C at atmospheric pressure. The gas from the dual fluidized bed is cooled, particle matter is removed by a cyclone before passing through a tar scrubber to remove tar from incomplete gasification. Removed particles, mainly unreacted fuel, is directed to the fluidized bed combustion reactor for combustion. There, also carbon deposited on the heat carrier surface is combusted for its regeneration and heating up. By looping this material back to the gasification reactor, the heat of combustion is supplied to the endothermic gasification reactor. The gas after tar removal is compressed, cleaned and further cooled before being sent to Fischer-Tropsch reactor. Here, the mixed gas containing CO, H2, and CH4 is used to synthesize hydrocarbons

in the presence of catalyst under appropriate conditions (see Chapter 5). After cooling, the product mixture is separated. Gaseous products are utilized in the combustion chamber, while the other stream is directed to the reforming process. In this process, the reactant hydrocarbon fuel (such as natural gas) reacts into hydrogen, carbon monoxide or other products at high temperature. The product was returned to the hydrocarbon synthesis. The Fischer-Tropsch-synthesis (FT) was selected for evaluation because this technology is used for synfuel production in commercial scale from natural gas and coal as gasification feedstock. The main difference to biomass as feedstock is the CO:H2 ratio, which needs to be adjusted by the water-gas-shift reaction, leading to the formation of additional CO2. For FT-synthesis, a CO:H2 ratio of around 1:2 is required.

5. Gasification BtL/PtL

In the dual bed gasification process described in the previous section, CO2 is generated in the gasification process i) by combustion reactions to supply process energy and ii) by the water-gas-shift-reaction to adjust the CO:H2 ratio for hydrocarbon fuel production. The CO2, generated in process (ii) usually is separated prior to synthesis, while that from process (i) usually is emitted after gas cleaning according to emission standards but can also recovered by a separation process. Additional hydrogen could be utilized to increase the product yield and reduce feedstock carbon loss.

To avoid the formation of CO2 in the water-gas-shift-reaction hydrogen could be introduced into the gasification reactor, in which by the gasification equilibrium reactions the CO:H2 ratio is adjusted as required for downstream synthesis. From process (ii), CO2 can be separated from the flue gas by available technologies and can be converted with renewable hydrogen by the reverse water-gas-shift reaction, which currently is under development (CO2 + H2 \square CO + H2O). This CO then, together with some more hydrogen, can be combined with the syngas from the gasifier for fuels synthesis (see Figure 11). That way, practically all carbon from the feedstock can be converted in to fuel carbon. The additional hydrogen required to achieve this can be provided e.g., by water electrolysis with renewable power.


Figure 10: Flowsheet of a BtL-process with dual bed gasification technology.

If this type of hydrogen or, consequently, power assisted BtL process (PBtL) is intended, another gasification process may be more efficient, but which is not investigated here in detail. If oxygen blown fluid bed or entrained flow reactors at are employed in autothermal operation with pure oxygen (to avoid nitrogen in the system), hydrogen can be added to the gasification reaction resulting in only little unavoidable CO2 formation by gasification reactions. From the very simplified equation C6H8O4 + 2 O2 + 10 H2,ext \square 6 "CH2" + 8 H2O it becomes clear that around 10 mol of hydrogen are required per formal molecular unit of lignocellulose. Around half of the oxygen by-produced in water electrolysis can be used in the gasification process.

6. Gasification for hydrogen

The objective of the above presented PBtL process is the maximization of hydrocarbon yield, leaving practically no CO2 for separation and storage. A maximum of bioenergy carrier is obtained at the cost of additions hydrogen supply. In contrast, also the complete conversion of the biocarbon to CO2 can be conducted, leaving hydrogen as the energy carrier produced.

Flow sheet in Figure 12 is the same as for the BtL process up to the water-gas-shift reactor. Here, all CO is shifted to CO2 and H2 by reaction with water. If the gasification is carried out with a liquid bio-feedstock at elevated pressure (e.g. the pyrolysis slurry as introduced in Chapter 1.2.4, further compression of H2 and liquefaction of CO2 could be performed with less energy efforts. Hydrogen is a demanded product with its high calorific value, high cleanliness, renewability, etc. Biomass is a resource with relatively low hydrogen content compared to natural gas and crude oil, however, in combination with the generation of negative emissions economic benefits may occur.





Figure 11: Flowsheet for power assisted synthetic fuel production.

7. Fast pyrolysis for bio-oil and bio-char

Biomass pyrolysis is a thermochemical reaction in which the macromolecules of biomass are decomposed in an environment of no or little air. It can be regarded as an independent process, including chemical bond breaking, isomerization, and polymerization of small molecules, etc., as well as an intermediate process during combustion, carbonization, liquefaction, gasification, etc., depending on the kinetics of the various thermochemical conversion. The main products of biomass pyrolysis are liquid bio-oil, combustible gas and solid biocharcoal. Biomass pyrolysis processes can be divided into slow pyrolysis and fast pyrolysis. In fast pyrolysis, large yields of bio-oil up to around 65 wt.% are obtained, while in slow pyrolysis the solid char yield is dominant.

The fast pyrolysis process was simulated based on bioliq® process at KIT (as shown in Figure 13 below) in this study. In this process, lignocellulosic biomass straw, was milled in a two-stage grinding mill and pneumatically transferred to a silo. In the twin-screw mixing reactor, the straw was mixed with an excess of hot sand for instant heat transfer. After pyrolysis reaction at 500 I the hot sand is separated from the product vapors and the very fine biochar and pneumatically transported to the sand silo for recycling. The resulting solid char is separated in a hot gas cyclone. The resulting hot steam is condensed in two stages.: (1) an organic condensate with around 15% is obtained at condensation temperatures of 80 - 90 °C, and (2) an aqueous condensate with more than 80 % water is recovered in case of the conversion of ash rich materials.





Figure 12: Flowsheet of gasification for hydrogen production with CO₂ capture.



Figure 13: Flowsheet of fast pyrolysis with CO₂ capture.



8. Slow pyrolysis for bio-char

Slow pyrolysis is a carbonization process for the production of charcoal, in which wood is heated in the absence of air to produce the charcoal, with yields reaching $30\% \sim 35\%$ of the feed mass. Slow pyrolysis occurs at 400-800 °C, with the heating rate below 10 °C/min (Jonsson 2016. Usually, coke and gas are produced in the slow pyrolysis process. Some of the gas can be condensed into a liquid fraction. The quantity of these products is affected by the type of feed and process conditions. In this study, the slow pyrolysis process was also simulated by the chemical simulation software Aspen.

For carbon capture and a carbon dioxide absorption unit was added to the process. Through the analysis and comparison of the simulation results, the influence of carbon dioxide absorption unit added to the slow pyrolysis process on the original process was obtained. In this study, a 50 MW slow pyrolysis process was simulated, as shown in Figure 14 below. This process refers to the slow pyrolysis unit of PYREG GmbH. The wood is reacted in a pyrolysis reactor at 450 °C to produce 25.1% gas, 44.3% liquid and 30.6% solid (data taken from (Martin 2010)). The solid and liquid products are separated from the reaction product. The gas was sent to the combustion furnace for complete combustion with air at 1150 °C, and the heat of the combustion product wis supplied to the pyrolysis reactor for pyrolysis reaction.



Figure 14: Flowsheet of slow pyrolysis with CO₂ capture.

The cooled combustion flue gas was re-cooled in a heat exchanger and then sent to the carbon dioxide absorption unit. The combustion product contains 15.3wt% carbon dioxide. The tail gas was compressed and sent to an absorber at 55.5 °C and 1 atm with 30% MEA solution as absorbent. The concentration of carbon dioxide in the purified gas was 10wt.%. After absorbing CO2, the rich liquid was pressurized and sent to the regeneration column, where CO2 was separated by desorption and emitted from the top. The regeneration is operated at 1.97 atm and 120 °C. The concentration of CO2 separated was 88.2 wt%. The CO2 absorption and desorption unit showed an energy consumption of 38.33 MW. The desorption tower had the highest energy consumption of 17.0 MW in the CO2 absorption and desorption unit.



1.5 Summary and conclusion

Bioenergy today contributes by 1 PJ to the around 11.8 PJ of the primary energy demand in Germany, providing 50 % of renewable energy. To produce heat and energy carriers from biomass, conversion processes are applied during which CO2 is emitted to different extent. To avoid its emission this CO2 can be separated by carbon capture processes from the various process streams for subsequent storage or utilization (CCS/CCU) of the so recovered green house gas. The combination of bioenergy with CCS is thus called bioenergy with carbon capture and storage, BECCS, consequently leading to negative emissions because CO2 is removed from the carbon cycle by that way.

Bioenergy is primarily used for heat and energy carrier production, which can be further converted into electricity, mobility and, again, heat. If biomass is combusted for heat production, CO2 can be recovered to a large extend by already established carbon capture technologies. The efforts to spend for this depend mainly on the scale of the combustion facility. In the production of energy carriers only part of the carbon contained in the feedstock is released mainly as CO2 during the production process and can be separated as well. The other carbon remains in the fuel and is only converted into CO2 when it is burned. If this happens in stationary systems, again CCS may become feasible. If combustion takes place in mobile applications, for example, in a car, the CO2 is considered irrecoverable in the context of BECCS.

As other CDR technologies, too, BECCS still is subjected to great uncertainties in terms of realistic potentials, possible environmental impacts, additional costs and other questions. For the future bioenergy use, however, CO2 extraction by BECCS may become decisive role, because a BECCS plant can delivers two products: energy and negative emissions. According to a given time and scenario, there may be a demand to prefer on relatively short term one product over the other one. The achievable span between both products for a specific technology depends significantly on the type of process and product produced. This trade-off is investigated in the HI-CAM project as part of the overall technology assessment on carbon dioxide removal options. In this report, technologies are identified, which are expected to be continued or may become relevant for bioenergy production in the next decades in Germany.

For BECCS, eight technologies have been considered for technology assessment with regard to their potential for negative emissions. Criteria for their selection were a high technology readiness level (TRL), available feedstock and products adaptable to the Germany energy system. They can be categorized into 4 main types of processes, which are biogas production for heat, power and SNG production, combustion for power and heat production, gasification for synthetic fuel production, and pyrolysis for biooil and biocoal production. In the following, the basic concepts of the selected technology scenarios, which were modelled to generate mass and energy balances, are presented.

Biogas firstly was considered in the "classical" heat & power application (CHP). Mesophilic anaerobic digestion was selected utilizing a mix of bio-waste, manure and purpose grown crops. The biogas, containing around 60 % of methane, is combusted in a 500 kWhel engine at 40 % electrical efficiency. The electrical power produced is fed into the public electricity grid. For CO2 capture, post-combustion chemical absorption by MEA as solvent is performed. Biogas, in the second application considered, is upgraded for injection into the public grid (SNG). Here, the raw-biogas needs to comply with the relevant regulations. In the technology scenario, a somewhat bigger, 1 MWth biogas plant is used. Separation of CO2 is first facilitated by water scrubbing at elevated pressure, after which raw SNG is further cleaned in an absorption column. For the grid injection, the SNG is pressurized and an odorant is added. Both biogas technologies are of TRL 9.

For biomass a power plant of 500 MWel with supercritical steam cycle was assumed, re-designed from formerly operation with hard coal. A location close the cost assures accessibility to cooling water as well as to lower cost imported biomass in form of fuel wood and residual lignocellulosic biomass.



CO2 is captured in a commercially available post-combustion amine-based absorption process. The around 10 vol.% CO2 content in the flue gas are recovered by around 90%. The plant's thermal efficiency with CCS is lower than that without CCS, as part of the heat produced are required to cover the energy demand for CO2 capture. In this case, the of thermal efficiency was estimated to fall to 33%.

For gasification, three process variants have been selected. The first one is the "classical" Biomass-to-liquids process, by which synthetic hydrocarbon fuels are produced from synthesis gas via the well-known Fischer-Tropsch process. To produce the syngas, woody biomass is gasified in a dual bed system consisting of a gasifier combined to a combustor in which the heat for gasification is generated and transferred by a solid heat carrier. The thermal fuel capacity was set to 200 MWth. CO2 may be obtained from two process streams: from the synthesis gas stream after water-gas-shift reaction and from the flue gas stream of the combustor. Roughly, one third of the feedstock carbon can be recovered from the fuel production process. In the second variant, CO2 emission during processing are omitted by addition of renewable hydrogen to the gasification process (PBtL). In this case, the feedstock carbon is retained nearly completely in the hydrocarbon product, but requiring substantial electrical power to produce hydrogen by water electrolysis. The by-produced oxygen could be used for gasification or in oxifuel combustion processes for more efficient CO2 removal from the flue gas. The third option aims at the production of hydrogen from biomass. Since biomass is a material low in hydrogen, this process may only become attractive when CCS creates added value. In this case, practically all feedstock carbon can be recovered from the process.

For biocoal production two types of pyrolysis plants of 100 MWth capacity were considered. Slow pyrolysis converts up to 70 % of carbon into the solid product, while the rest is released as CO2, CO and some other volatile gases. Although biocoal may be used as carbon material or energy carrier, it is considered for long-term soil applications due to its relatively high stability due to production temperatures above 500 °C, for example, in a rotating drum reactor. At the same temperature, fast pyrolysis may be applied. Here, the finely grinded biomass is heated rapidly by a solid heat carrier, reacted within a few seconds after which instant cooling leads to a 60 – 70 wt.% of liquid condensate. This biooil can be used as heating oil or may be upgraded to fuels by hydrotreating. Around 20 wt.% of the feedstock remains as biocoal including the minerals content of the original biomass. Volatile carbon compounds from slow and fast pyrolysis are combusted to produce the heat required for pyrolysis, after which all remaining carbon can be recovered as CO2.

If BECCS should be implemented according to the global climate protection scenarios, high-capacity carbon capture plants needs to be installed and operated within the next ten to twenty years. Also, the infrastructure for CO2 transport and storage or its utilization would have to be established. When discussing future bioenergy development, BECCS therefore should be considered as a near-term technology option.



2 DIRECT AIR CAPTURE (DAC)

Dominik Heß, Roland Dittmeyer

Processes called Direct Air Capture, or short DAC, are technological solutions to filter CO2 from the atmosphere. The systems use specific chemical interactions of the CO2 with special materials to bind it and therefore remove the greenhouse gas from the air. DAC-processes generally function as a two-step process: capture and regeneration. While capture, air is moved along the specialized material, called sorbent. This sorbent can either be a strong alkaline solution or a solid. Only the CO2 reacts with the sorbent and forms covalent bonds, while most other components of the air, like nitrogen or oxygen, are inert to the sorbent. In case of Low-Temperature DAC, water can be Cocaptured and used for hydrogen production or orher purposes. This chemical reaction is very specific and therefore enables the separation of almost pure CO2 although the concentration in air is really low at 400 ppm. The CO2-depleted air lefts the DAC-unit and the loaded sorbent is left behind. With time, the sorbent is loaded with more and more CO2 until there are no bonding places are left to react. Before a complete loading is reached the DAC changes to the regeneration step and the flow of air is interrupted by closing the chamber or moving the sorbent unit to a regeneration system. To release the CO2, the strong bonds between the gas and the sorbent must be broken. For that energy in form of heat is required to reverse the exothermal capture reaction. Depending on the used technology, different temperatures are required. While regeneration, the CO2 is harvested and can be processed further. The regenerated sorbent can be fed into the capture step and undergo a new cycle. A schematic is shown in Figure 15.

Currently there are two main technologies on the edge of commercial development, while other approaches are in an early R&D-state. The most promising approaches are discussed in the following chapter.



Figure 15: Schematic of the DAC-process with the two steps of capture and regeneration. (HI-CAM 2020)



2.1 Low-Temperature-DAC

The Low-Temperature-DAC-approach (LT-DAC) uses a solid amine-based sorbent to bind the CO2 form the air. The gas reacts with amine groups at the surface to form a chemical bond (chemisorption). The capture step is executed at ambient conditions. Beside the CO2, moisture from the air is captured as well, which could be used in later applications, e.g. hydrogen production. The sorbent is either composed of small beads in a loose bed or on form of a monolith. Regeneration is done by lowering the pressure and increasing the temperature, usually by using steam at around 100°C. The steam concurrently bonds to the surface and delivers the energy to break the bonds. CO2 and water can be separated by condensation and drying. The regeneration step is with around 15min a lot faster than the capture process, which has to be considered in applications. (Climeworks 2020b; Global Thermostat)

The system needs electric energy for air movement as well as heat for the regeneration. Due to the low temperature, a lot of waste heat sources could be used. The main manufacturers of this process are Climeworks and Global Thermostat.

2.2 High-Temperature-DAC

A second approach to harvest CO2 from the air, is the high temperature-DAC (HT-DAC) approach. Here, a strong basic solution, e.g. potassium hydroxide, is used to capture the CO2. The solution is finely dispersed in the air to enhance the available surface area and decrease material transport limits. In a chemical reaction happening in the capture unit, potassium carbonate is formed, which stays dissolved. In an intermediate step this potassium carbonate reacts with calcium oxide to form solid calcium carbonate and dissolved potassium hydroxide. This pellet reactor marks the border between the capture and regeneration cycle. The potassium hydroxide can be reused in the air contactor, while the calcium carbonate is transferred to the calciner. Here, the solid is heated to 900°C. At this high temperature the material breaks down into the original compounds calcium oxide and CO2. The CO2 is discharged into the conditioning process and the calcium oxide can re-enter the regeneration cycle. The high temperatures must be provided by burning natural gas, at the moment. A purely electric system is under development. The CO2 produced for heating is captured as well, but lowers the overall efficiency. The biggest and only commercial company for this technology is carbon engineering. (Keith et al. 2018)



Figure 16: Schematic of Carbon Engineering's HT-DAC process. (Carbon Engineering 2020a)



2.3 Electro-Swing-Adsorption

A novel approach to DAC is the electro-swing-adsorption (ESA), where an electrochemical cell is used to bind the CO2. The system is constructed similar to a traditional battery. The two electrodes consist of specialised materials. While capturing the outer layers react with the CO2 from the air. The inner material is never in contact with the air and only serves the purpose of equibrilating the electric charges. If polarity is reversed, CO2 is released. The process has the potential to be especially energy efficient, but is a very early stage. A schematic is shown in Figure 17. (Voskian und Hatton 2019; Eisamann et al. 2009) A secondary approach to electrochemical CO2 capture from air is an electrodialysis cell. Here a capture solution is used, similar to the HT-DAC approach, but instead of heating, the saturated solution is regenerated in a electrodialysis cell, enabling a continuous process with potential efficiencies similar to the fuel cell approach. (Eisamann et al. 2009)



Figure 17: Schematic of the ESA-process (Voskian und Hatton 2019).

2.4 Key figures Technology

2.4.1 Readiness Level (TRL)

The different DAC-Technologies could be divided into two groups, regarding the readiness for large deployment. LT and HT-DAC solutions are in the edge of commercial finalization, while others are in an early development stage. Approaches like ESA or crystallisation-processes are proven to function, but are far from broad availability, due to high cost of low volume production and the still high price for special material, such as the sorbent of ESA. (Fasihi et al. 2019)

LT-DAC has left the early stages of development and is ready for a wider application. There are currently two main players in the market. Climeworks from Zürich in Switzerland is a spinoff of the ETH Zürich and has developed a LT-DAC adsorption process. It uses a polymer-based amine sorbent, which can be produces at



reasonable prices and at high quantities. A second company is Global Thermostat, based in the US, with their own LT-DAC-System. They use a polymer-sorbent as well, but instead of a bulk of small beads like Climeworks, they use a microstructured monolith. This lowers the pressure drop, while increasing the capture rate. Another main difference is that Climeworks is using one chamber to host both the regeneration and the capture. This leads to a cyclic process where there are phases of capture and phases of regeneration. A continuous production of CO2 is not possible in this system. The process of Global Thermostat uses two separate chambers for the steps, generating a continuous process. The difficulty here is that the sorbent has to be transported between the chambers, complicating the mechanics of the system. (Heß et al. 2020)

Both companies are currently deploying their solution in projects on a larger scale. Global Thermostat deploys their technology in cooperation with Porsche and Siemens Energy Solutions at the border of Chile, where they use cheap wind energy to produce Methanol and Gasoline substitutes via the MtG-process with CO2 from the air. Climeworks is building a CO2-sequestration plant in Island, using geothermal energy, while the consortium Norsk e-Fuel will produce PtL-fuels in Norway, using hydropower and a combination of DAC and point source CO2. (Norsk e-Fuel 2020; Climeworks 2020a; Siemens Energy und Porsche)

The HT-DAC solution from Carbon Engineering is in a comparable state. The technology is proven to work in a pilot plant in Squamisch. Based on data acquired from this pilot, carbon engineering is planning a 1Mt capture plant in Texas to provide CO2 for EOR. The difference is that the HT-DAC solution has not been sold to customers so far. This is because the technology cannot be scaled down and is therefore unable to provide small modules for individual customers. The large project format is the only suiting deployment strategy for HT-DAC. (Carbon Engineering 2020)

Overall, the LT and HT-DAC technologies could be considered TRL 7 or 8, while ESA is still more in the range of 6 or 7. As soon as the big projects are functional, one could argue if TRL9 is reached by then.

2.4.2 Energy Demand

The energy demand for DAC is highly influenced by the regeneration step. While only a small proportion of the required power is electrical, for the pumps and fans, the major part is heat. This thermal energy is used to regenerate the sorbent and therefore release the CO2 from the carrier material. While this heat is delivered at 100°C for LT-DAC, HT-DAC needs up to 900°C and has therefore very limited options for the heat source. The key data are given in Figure 9 for the main technologies, as stated by the companies. The numbers include the work for compression or liquefaction, which can be estimated to 100 kWh/tCO2. (Ausfelder und Bazzanella; Jackson und Brodal 2019). In general, the energy demands of the technologies are very similar. Even the differences in electrical power consumption are close. The LT-DAC solution from Global Thermostat has the potential to be slightly more energy efficient due to the low pressure drop monolith design and the efficient regeneration. The numbers are ambitious, but have to be proven in a real use case. Apart from those differences, the figures are closer than one might expect. Even the HT-DAC solution has a comparable energy demand, but the required temperature makes it difficult and today impossible to provide the heat in a regenerative and environmentally friendly way. Today, natural gas has to be burnt to reach the high temperatures. A purely electric system would render the co-capture of those flue gases unnecessary, increasing the efficiency. Further research and development is needed to reach such a system. Since then, it will be dependent on possibly fossil natural gas.



Manufacturer		Carbon Engineering	Climeworks	Global Thermostat
Technology		HT-DAC	LT-DAC	LT-DAC
Energy demand	electric	366 (1500*)	200-300	200
(kWh/tCO₂)	thermal	1458 (2448**)	1500-2000	1170
Cost 2050 (now) (USI	D/t _{co2})	64-232 (<250)	<100 (600-800)	50 (<200)

Table 9: Key facts of different commercial DAC-solutions. (Heß et al. 2020)

2.4.3 Cost

The cost for the captured CO2 range today from 200 to 800\$ per t of CO2. The expenditures range widely due to the different TRLs and the different strategies the companies follow. The higher estimates are made by Climeworks for their container-based module. This is a rather small sized unit, which is available today. Therefore, capturing CO2 is relatively expensive, because there could not be taken advantage of scaling factors or mass fabrication. The lower estimates of today's capture cost are made by Carbon Engineering and Global Thermostat. They calculate their cost based on their current ongoing projects. Those are in a larger scale and therefore the cost could be decreased drastically by exploiting benefits of mass fabrication and scaling effects. This and low energy prices of renewable electricity, will lower the price for DAC down to 50\$/tCO2 until 2050 in accordance with the manufacturers. Desorption temperatures could also decrease to as low as 45°C, claimed by Global Thermostat, enabling more waste heat sources. Most DAC projects are coupled with PtL or storage solutions, which makes the energy supply the major cost factor. Therefore, the interest is high in large scale plants with cheap renewable energy, while small scale systems are not yet in the focus, they could provide, if manufacturing is getting less expensive, a viable solution for a wide spread use of DAC.

2.4.4 Area Demand

The land use of DAC is inherently small, because it is an industrial plant and no biological or geological factors need to be accounted for. In terms of CO2 capture capacity, DAC is often compared to biological solutions, like BECCS. In a direct comparison, meaning the pure CO2 uptake per area, DAC is around 40 to 65 times more efficient. If energy is abundant, DAC is therefore the solution with a considerably lower land impact. Furthermore, DAC does not require special land and especially no fertile soil. A direct competition to food production is not given. If energy consumption for DAC is integrated, the numbers change drastically. If the energy demand is provided by solar energy with an area demand of 28 to 64 km2 per TWh of energy per year (Evans et al. 2009), the area for DAC increases to 40 to 160 km2/MtCO2. While those demands are still considerably lower than the numbers for plant-based systems (compare table). Since both solutions will be needed for a Net-Zero Germany, DAC should be installed in areas without fertile soil or integrated in other systems and therefore create to land use at all.



	Corn	Rain forest	Tempered forest	DAC	BECCS*
Area demand km2/ MtCO ₂	329	270	390	7-8,4	424-450
Area for 1 GtCO₂/a in km2	328.785	270.000	390.000	7.000-8.400	424.000- 450.000
Area equivalent to	Finnland	Großbritan- nien	Deutschland	Großraum London	Kalifornien/ Schweden
Reference	(Deutsches Mais- komitee e.V. (DMK); Wörde- hoff et al. 2012; Schink)	(National Academies Press (US) 2018)		(Creutzig et al. 2019)	

Table 10: Area demand of different CDR-measures without energy production. (Heß et al. 2020)

2.4.5 Scalability

The DAC-solutions differ widely in terms of scalability. The least flexile technology is HT-DAC. The high-temperature approach is only feasible in large industrial scales to run efficiently. Small plants could not handle the high temperatures needed for this process. Furthermore, skilled labour is required to operate these facilities. The process is a rather classical chemical process and benefits therefore from scaling effects. From investment cost to labour intensity, all those will shrink, when the plant grows.

LT-DAC is a lot easier to scale down. The sorbent consists of small beads in bulks or microstructured monoliths, which are parallelized to achieve bigger process scales. The size of those sorbent chambers can easily be reduced, by adding less beads or cutting the monolith. The production costs are still considerably higher at small scales, but could shrink a lot if mass fabrication and novel production methods, like additive manufacturing, are introduced. In theory, small plants are feasible. Climeworks started their manufacturing in containerbased modules, due to the ability to stack them at wish, proofing the capability of smaller systems.

Novel DAC-approaches, such as ESA, also promise small-scale capabilities. The cells could be stacked, similar to lithium batteries and nearly unlimited sized, by parallelisation or bigger cell sizes. If heat management is taken care of, ESA could also be a very flexible solution for DAC. (Heß et al. 2020; Global Thermostat; Climeworks 05.09.2019)

2.5 Integration into urban scenarios

2.5.1 Decentralized or Semi-Central Scenario

To further reduce the impact of DAC, regarding land use or energy consumption, small scale DAC-plants could be integrated into HVAC (heating, ventilation and air conditioning)-systems on larger office and retail buildings. Since a big portion of the electricity consumed by the DAC is due to the air movement, a synergy could be achieved. The low concentration of just 400 ppm of CO2 in the air makes it necessary to move around 1,3 million m³ of air to capture one ton of CO2, even at a capture rate of 100%. Especially the low pressure-drop-system of Global Thermostat could be integrated in ventilation systems without compromising the function, and without increasing the energy consumptions of the fans considerably.



After the CO2 is captured, it has to be processed in some way. This use of the CO2 heavily influences the size and composition of the whole system. In a completely decentralized system, the CO2 is converted on site to more useful or storable products, such as hydrocarbons or fuels. For this purpose, hydrogen is produced at site to create syngas as feedstock for more useful and valuable products. Those could be stored at site and used later or sold to the market. Products like synthetic natural gas (SNG) could be inserted into the existing gas grid. The size of this plant would be heavily dependent on the energy supply. A decentralized and autonomous plant, would use renewable energy, produced at this very site via photovoltaics (PV), e.g. building integrated PB (BiPV). However, it is likely, that the energy produced will not be sufficient to power both, DAC and the conversion scheme.

For this reason, a Semi-Centralize-solution is imaginable. In this option, only DAC would be installed in the ventilation system at the buildings. The CO2 would be transferred to Semi-Centralized conversion plants, where either hydrogen is delivered by pipeline or energy is produced. Small distances to renewable energy sources could be bridged by transporting the electricity, the hydrogen or the CO2 to the conversion plant. Because the CO2 must be collected from the buildings anyway in this scenario, a transportation a few kilometres further instead of transporting the electricity with losses seems to be the more sensible solution.

2.5.2 Large scale Scenario

Apart from the decentralized and semi-central solution, large-scale application of DAC combined with storage or utilisation schemes could complete the net-zero plan. In large-scale applications, HT-DAC-systems could have benefits over the LT-DAC-system due to well-proven technologies and the relatively cheap sorbent. Additionally, if the high temperature heat could be provided via solar thermal energy generation, e.g via concentrated solar power (CSP), a highly efficient DAC is possible. In a large scenario, scaling effects could lower the prices. Where small solutions are still in development, the companies aim for large applications anyway. Therefore, if unoccupied land and energy supply allow a DAC plant in addition to the urban integration, it is sensible to go for a big plant.

2.5.3 Automation and Hazards

If a DAC system should be operated in an urban and civilian scenario, it needs to be automated. There cannot be permanent staff present to run the DAC system. This fact favours the LT-DAC-system or ESA. The adsorption has few moving parts or complicated chemical stages. Additionally, the solid sorbent cannot leak or get damaged in the closed chamber. Therefore, only the periphery like pumps or vents are prone to wear and environmental influences. The system can be automated in small scales and checks in regular intervals by skilled professionals. Sensors and a smart programming could also predetermine upcoming maintenance issues to call for a worker, before the plant must shut down.

The hazards of DAC plants are of special interest in case of urban scenarios, because here untrained persons encounter the plants. Additionally, due to the autonomy of the system, there are long periods without supervision of skilled personnel, which could create dangers in case of an emergency. Fortunately, there are not a lot of dangers tied to running a DAC-plant. There are no poisonous or corrosive materials used. Only the moderate high temperatures pose some risk in addition to the elevated pressures of the conditioned CO2. If the CO2 is liquefied, there is an additional hazard of freezing injuries caused by very low temperatures. Other from that, electricity poses a general risk, not greater than in standard installations. Overall, there are no hazards, which complicate the use of automated plants in urban scenarios.



2.5.4 Maintenance

Due to its simplicity, LT-DAC solutions are low in maintenance, because there are no corrosive materials or other high wear parts. Only the sorbent loses its capacity. Every few years, the sorbent material must be renewed. Therefore, the plant must pause and technicians change the module or the bulk. Other from that, only the pumps ventilators and vents must be checked for wear and failures. The plant has a comparable maintenance effort like usual ventilation systems or heating systems and is therefore able to be implemented into urban areas.

2.5.5 Example case

As one example for an urban integration of DAC in a HVAC-system, the Fair Tower in Frankfurt am Main is analysed. The authors of the "Crowd Oil"-paper use this building to state the potential of those integrated systems and is a typical big office building. The 257m high building has an office area of around 62.000 m2 and is located near the fair area in Frankfurt. (Messeturm Frankfurt)

Total energy demand

Calculated with the recommended air exchange rate of 5 to 10, the ventilation system pumps 1 to 2 M m3 of air per hour and could therefore provide around 0,75 to 1,5 tCO2 per hour. With an estimated electricity demand of 300 kWh/tCO2 and a heat demand of 1500 kWh/tCO2 a constant power supply of 225 to 450 kW with a heat stream of 1.125 to 2.250 kW is needed. This equated to a yearly capture capacity of 6.500 to 13.000 tCO2, which can be processed further. If on site conversion is installed, most of the heat could be provided by the synthesis for the LT-DAC system. This would drastically reduce the need for a heat source, but would require a lot of Hydrogen to be produced at site or imported into the building. If a hydrogen-grid or powerful electricity grid is reality in the future, on site conversion will be a viable option. (Dittmeyer et al. 2019)

Infrastructure for CO₂

The produced CO2 can be converted into liquid hydrocarbons or other products such as Methane on site or transported to a more centralizes conversion plant. If this is the case, the CO2 needs to be transported out of the building. In case of the Fair Tower, the captured CO2 equated to 5.500 to 11.000 m3 of liquefied gas. Transported in tank containers with an average capacity of 20 m3 this would lead to 280 to 550 trucks a year, transporting the CO2 to conversion sites. So more than one truck a day. If there is enough space available in a garage or similar structures, a few containers might be stored to reduce the frequency of collection to once or twice a week. At this size of a building, pipelines seem to be a viable solution as well, if a direct conversion is not feasible, to reduce the effort of transporting the liquid CO2. Smaller office buildings might also be able to transport their CO2 with one container a week, which would be a sensible frequency.

2.6 Conclusion

There are different DAC technologies available for theoretical DAC-plants in urban areas. The LT-DAC and HT-DAC solution are both suitable for a larger scale implementation. The decentralized approach favours the LT-DAC-system, because it has some benefits. At first, the HT-DAC is not scalable enough to fit into a HVAC or ventilation system. The classical chemical process is meant to exist on larger scales. Additionally, HT-DAC requires the handling of hazardous chemicals, which is not the case for LT-DAC; hence, it is a lot easier to automate. Additionally, the low-pressure drop eases the installation in existing ventilation systems, without compromising the function of the existing fans. With the addition of LT-DAC in HVAC systems, a scheme without compromises for the end consumer could be build, which is the main goal of the project. Other technologies lack the easiness or readiness to provide such a system. Therefore, the choice is on LT-DAC-solutions.



3 SYNGAS PRODUCTION

Enric Prats, Nathalie Monnerie, Dominik Heß, Roland Dittmeyer

CO2 is a chemically unreactive substance. Therefore, it needs to be activated, before it can be processed into hydrocarbons and fuels. This is achieved by converting it into carbon monoxide, a highly reactive gas, which can be used in a gas mixture, called syngas. Syngas is a combination of hydrogen and carbon monoxide in variable portions, which acts as a basis for producing a variety of products. In this report, the synthesis of methane, methanol and Fischer-Tropsch-Product is investigated. All reactions use syngas as educt in different rations of hydrogen to carbon monoxide (comp. Table 11). To produce the syngas, different processes are available. In this report, three processes are compared: Solarthermal process, PEM- electrolyses with rWGS and SOEC Co-Electrolysis. All of the different paths are simulated on a basic level using Aspen Plus to compare the idealized technologies. In reality, lots of influencing factor will lover the efficiencies, but for a better comparability, those factors are not accounted for in this report. All syngas is delivered at 50 bars and 25 °C.

Table 11: Ideal syngas-ratio for the different product synthesis, derived from the stoichiometry

Product	Methanol	Fischer-Tropsch	Methane
H2:CO-ratio	2:1	2,26:1	3:1

3.1 Thermochemical Syngas Production

3.1.1 Process description

A well-known way to produce fuels is using water and/or carbon dioxide as raw materials to split them and obtain hydrogen and/or carbon monoxide respectively. However, these molecules are extraordinarily stable and their decomposition is not thermodynamically favoured even at temperatures as high as 3000 °C (Miller 2007).



Figure 18: Schematic representation of a TCC, consisting on a redox reaction involving a metal oxide pair (depicted as MOox/MOred) to produce hydrogen (H2), carbon monoxide (CO) or both (synthetic gas). Extracted from (Agrafiotis et al. 2018).



Solar thermochemical cycles (TCC) are suggested as a promising alternative that require lower temperatures to perform the water or carbon dioxide split reaction. As shown in Figure 18, TCC follow a redox reaction scheme and involve a metal oxide redox pair.

The first reaction is an endothermic thermal reduction carried at a high temperature and which can be driven by concentrated solar power (IEA 2010), while the second reaction is an exothermic oxidation carried at a lower temperature (Agrafiotis et al. 2018). It must be also noted that oxygen and hydrogen or carbon monoxide are produced separately, so that no additional separation step is further needed and thus avoiding otherwise potentially dangerous reconversions (Miller 2007).

Depending on the metal oxide used, TCC may fall in two categories: volatile and non-volatile cycles. In the former, the reduction temperature is higher than the melting (or even boiling point) of the oxidized metal, which increases the complexity of the system due to vaporization and recombination issues. Therefore, the latter type has received most of the scientific attention (Agrafiotis et al. 2018). For non-volatiles cycles, which remain in solid phase through the cycle, four main families of compounds are considered of interest: ferrites (Tred \approx 1300-1400 °C), ceria compounds (Tred \approx 1500 °C), perovskites and hercynites. For most compounds, Tox is between 700 and 1000 °C (slow kinetics are reported at lower temperatures) (Agrafiotis et al. 2018).

Significant efforts are being made on developing and optimizing reactors that can host the aforementioned reactions so that this technology could become commercially available in the future. Several criteria must be observed when designing TCC reactors.

Firstly, an optimal arrangement should be found to use the maximum available sun radiation. Depending on the type of cycle, literature suggests designs of solar reactors performing only the reduction step (volatile cycles) or hosting the two steps of the cycle (non-volatile cycles). For the latter, solar reactors based on ceramic monolithic honeycombs (Säck et al. 2016) and ceramic foams (Romero et al. 2019) have shown interesting results and are currently under optimization (Agrafiotis et al. 2015). Additionally, these designs must be coupled to the available solar concentrating technology (further explained in section 3.1.2), although indirect approaches have also been suggested (Agrafiotis et al. 2018).

Secondly, TR strongly depends on oxygen partial pressure, with enhanced performance at low values. These values may be achieved with sweep gases other than air (e.g. nitrogen) or vacuum (Rytter et al. 2016). Remarkable achievements have been recently reported that take advantage of certain metal oxides to remove oxygen from gas mixtures via temperature and pressure swing adsorption. Such processes are claimed to be less energy-intensive than cryogenic distillation (Bulfin et al. 2019).

Finally, several studies confirm that adequate heat recovery is also a parameter of major relevance (Rytter et al. 2016; Bader et al. 2013). This recovery is mostly focused on heat exchange between oxidized and reduced metal oxide streams and between reactor's inlets and outlets. Research on this topic is currently on-going (Holzemer-Zerhusen et al. 2021).





Figure 19: Schematic block diagram showing integration of solar fuels produced by TCC in the energy system. Note the carbon circularity of the process. Extracted from (Roeb 2019).

Hydrogen produced in solar TCC can be directly used as a fuel, but it is also possible to obtain synthesis gas by one of the three possible pathways (Kim et al. 2012): H2 production followed by reverse water gas shift (rWGS) with CO2, CO production followed by water gas shift with H2O or by (simultaneous) splitting of H2O and CO2. Both hydrogen and synthesis gas can be directly injected at a certain extend on natural gas pipelines without requiring any modification of the grid (IEA 2010).

Furthermore, synthesis gas can be reformed with mature technology towards methanol (Monnerie et al. 2020), dimethylether (Miller 2007) and other valuable liquid fuels such as gasoline, kerosene or diesel (Pregger et al. 2020) via Fischer-Tropsch synthesis. These options can be fed to currently available vehicles with some minor changes or even directly, hence fostering the transition. Figure 19 illustrates the integration of Solar TCC to the current energetic needs.

Several authors have studied the relevance of solar fuels produced by TCC (IEA 2010; Bader et al. 2013; Stechel und Miller 2013). Some of the two most critical parameters to determine whether the present approach could become a feasible solution to produce carbon-neutral fuels is the sun-to-fuel efficiency and the levelized cost of fuel, which are, in fact, closely related. The former is defined as the higher heating value (HHV) of the produced fuel divided by the solar power input of the cycle (Bader et al. 2013). While the latter is the production cost of this fuel considering the facility's initial investment and lifetime, but also other factors such as the financial discount rate or the plant's capacity factor (IEA 2010).

Sun-to-fuel efficiencies above 10% are considered promising because such plants would require smaller solar fields and, according to several technoeconomic assessments (Kim et al. 2012; Monnerie et al. 2020; Moser et al. 2019), these sunlight collecting systems account for the highest share of the initial investment. Therefore, higher sun-to-fuel efficiencies, combined with lower manufacturing costs of heliostats and receivers, would lead to lower levelized cost of fuel. Consequently, more competitive market selling prices should be possible for solar fuels.

3.1.2 Concentrated solar power

Concentrated solar power (CSP) is a renewable energy that uses sunlight as a heat source, whereas photovoltaics directly uses the energy of photons. In order to increase the possible temperatures that can be reached with solar radiation, sunlight is concentrated by mirrors towards a receiver where a heat transfer fluid (HTF) is warmed up. HTFs are typically steam, molten salts or air. On the one hand, steam can directly drive a power block to produce electricity, while the molten salts are either stored in a heat storage system or used to trans-



fer energy to another working fluid, which can be used in a power block. On the other hand, pressurized air is heated in the receiver and directly used to propel a gas turbine. The remaining heat is then used to produce steam that would impulse a second generator. This technology is also known as solar-based Brayton cycle.

Although electricity production is one of the main applications of CSP, the possibility of supplying large quantities of heat at extremely high temperatures is an attractive feature for many chemical processes such as synthetic fuels production.

Nowadays, four main CSP technologies exist depending on the arrangement between reflectors and receivers as shown in the figure below. On the one hand, parabolic troughs and linear Fresnel reflectors rely on a linear focus approach, in which the sunlight is concentrated between 40 and 100 times and reflected in a linear receiver that contents an HTF. On the other hand, the parabolic dish and the central receiver are point focus approaches that concentrate the sunlight between 100 and 2000 times towards a single point. Due to their higher concentration ratios, higher temperatures are often achieved and therefore, they are preferred for synthetic fuels production (IEA 2014).

Concentrated solar power cannot use diffused sunlight and therefore, its performance is strongly determined by direct normal irradiance (DNI). Consequently, locations with higher DNI values are preferable such as arid and semi-arid regions with consistent clear skies, which are often found between 15 and 40° in both hemispheres. From these, Middle East and North Africa (MENA) represents an excellent region to use the CSP technology, and is thus, a potential solar fuels exporter.

Thanks to the technological advances achieved in the last decade, LCOE produced with CSP is starting to be able to compete with fossil fuels and, if combined with heat storage, it can provide synergies with other renewable energies such as PV or wind power to cope with peak demand and intermittencies. Therefore, it seems safe to state that CSP will gain importance in the future energy-mix (IRENA 2020).



Figure 20: representation of the several available CSP technologies depending on their receiver and reflector arrangement. (World Bank 2021)



3.1.3 Syngas production

In the model produced for the present work. The chosen metal oxide is ceria oxide, since it is one of the most promising cycles including successful scale-up to pilot plant size (Romero, 2019). Following the valuable experience of Romero et al., the oxidation reaction will be performed at 900 °C, while the reduction will take place at 1500 °C. In the same study, recommended pressure conditions are 1 bar and 10 mbar absolute pressure for oxidation and reduction reactions respectively. The use of vacuum replaces the sweep gas, but given that interesting advances have been recently published regarding low-cost production methods for sweep gas (Bulfin et al. 2019; Brendelberger et al. 2019), this approach will be used instead of vacuum.

The process layout selected for the proof-of-concept deliverable is shown in Figure 21, although different layouts have also been considered in literature (Kim et al. 2012; Rytter et al. 2016). As it can be seen in the flowchart, steam and CO2 are mixed with cerium(III) oxide (Ce2O3) in reactor where the exothermal oxidation reaction takes place. Then, the gas outlet stream undergoes adequate separation and recycling of unreacted materials while cerium dioxide (CeO2) is fed to a reduction reactor where, thanks to concentrated solar power, oxygen will be released and removed with nitrogen. Finally, sweep gas is purified and oxygen is obtained (Monnerie et al. 2020).

Since syngas is only produced during daylight, it is compressed to 50 bar at the end of the process and stored in a tank in order to allow around-the-clock fuel production downstream.

3.2 Combination of PEM-Electrolysis and reverse-water-gas-shift

A second and relatively established way of producing syngas is the combination of PEM (proton exchange membrane)-electrolysis and reverse water gas shift (rWGS)-reaction. In the first stage, liquid water is split by applying an electrical current via two electrodes, which are typically coated in platinum.



Figure 21: Chosen process layout for the solar thermochemical cycle. The energy streams have been removed for simplicity.





At the anode, the liquid water is split into hydrogen ions, oxygen and free electrons, which can travel through the electrode to the power supply. The protons diffuse through the eponymous proton-exchange-membrane to the cathode, where they are recombined with the electrons to form gaseous hydrogen. The process is typically executed at room temperature at arbitrary pressure. The process is suited well for the targeted small-scale application in buildings. The plants are easy to handle and have low maintenance requirements. Alkaline electrolysis (AEL) can reach similar efficiencies as PEM, but only at larger scales with the use of hazardous chemicals, which compromises the use without trained personnel in residential settings. Therefore, this report concentrates on PEM as source for hydrogen. (Tom Smolinka et al. 2018)

This hydrogen can be used in a reverse-water-gas-shift-reaction to form syngas. In this reaction, hydrogen reacts with CO2 to form CO and water:

$$H_2 + CO_2 \rightleftharpoons CO + H_2O$$
 $\Delta H_{300K} = 41,21 \frac{kJ}{mol}$

Figure 22: Endothermic rWGS-recation for the syngas production (Ott et al. 2000)

Due to its endothermic nature, a high temperature is favorable to increase the CO output. Additionally, the concurrent methanation-reaction is hindered at high temperatures, which is why the rWGS-reaction is executed at temperatures of around 900 °C (Daza und Kuhn 2016). Since all components are gases, no change in the amount of substance takes place and the pressure does not influence the equilibrium. The pressure is set at reaction conditions of the downstream synthesis, if a recycle is fed before the rWGS-reactor. In this report, the pressure is set at atmospheric conditions. The formed water is either collected for later use or refined and fed back in to the electrolysis. This is only possible if both reactors are situated at the same plant. If hydrogen is imported from outside, there is wastewater to be treated. The schematic of the process is shown in Figure 23. For the simulation, the PEM-electrolysis is modelled by a stochiometric reactor, where all the water is split into hydrogen and oxygen isothermally. The required electricity is obtained by the calculated heat stream into the reactor. The rWGS-reactor is an equilibrium reactor operated at 850°C and ambient pressure. The unreacted CO2, the formed water and the required amount of H2 for the rWGS-reaction is recycled. Separation takes place by a separation unit, which executes an idealized separation, while a calculator block organised the correct amounts for the recycle. The syngas is compressed and cooled before the output.

108

0.333

-0.962

100

0.307

-0.806

Parameter	Units	2:1	2.26:1
CSP required (T > 1500 °C)	kJ / mol SG	402	402
High pressure steam produced (250 °C)	kJ / mol SG	86.6	88.7

kJ / mol SG

mol CO2 / mol SG

mol H2O / mol SG

Table 12: Results of the basic model showing required energy at different H2:CO- ratios. SG=Syng
--

Electricity required for compressors

CO2 input required

Water input required

3:1 400

93.1

84.8

0.250

-0.471



3.3 Direct Co-Electrolysis of water and CO₂

A third way of generating syngas is by utilising the steam-electrolysis. Here, water vapour and CO2 are fed into a solid-oxide-electrolysis-cell (SOEC) at high temperatures of around 850°C. The membrane must consist of a ceramic substance to withstand the enormous heat. The work principle is comparable to the PEM-electrolysis. The difference is, that alongside the water splitting, an rWGS-equilibrium is generated, which produces carbon monoxide. This equilibrium is, like in the rWGS, temperature driven. To simulate this behaviour, a primary stack (stochiometric reactor with conversion of one), similar to the PEM-reactor, splits the CO2, followed by an rWGS-step (equilibrium reactor). After that, the formed water from the rWGS-equilibrium is split again in a second stack, so no water exits the SOEC. Unreacted CO2 is



Figure 23: Schematic of the syngas production via PEM and rWGS.

recycled and the correct syngas mixture is separated into the conditioning stream, with the composition derived from a calculator block. The syngas is conditioned to the required temperature and pressure and then exits the plant. The flowsheet is given in Figure 24.

3.4 Energetic Analysis and comparison

To assess the different options for syngas production, for every version an energetic analysis in form of a pinch-analysis was made. Here every heat stream is integrated and an ideal heat exchanger network is generated, minimalizing the required external cooling or heating power. These additional utility streams are needed to fuel the process. The results are given in normalized on the amount of substance of the produced syngas. Since this is a basic and ideal





Figure 24: Schematic of the syngas production via SOEC Co-electrolysis

simulation, the size of the plant does not change the normalized values. It is clear, that the solar thermal approach has a drastically lower energy consumption than the other paths, since most of the energy is harvested at site from the sun. This is also the reason, why almost no additional heating is required, while this process even produces waste heat. The main energy source for the electrolysis driven processes is electricity. This can come from installed PV panels directly on site or, more likely due to the huge energy consumption, from the grid. Since most of the energy is used to produce hydrogen, it is also possible to use imported hydrogen to fuel the processes. Since a gas is relatively efficient to transport, it could help increase the overall efficiency. The numbers state clearly, that if possible, a direct implementation of CSP to produce syngas is preferable to the electrolysis solutions. If this is not doable, the other pathways seem reasonable. The SOEC has the potential of being more efficient in reality plus reducing the complexity of the chain by removing one consecutive step. If hydrogen is to be imported into the facility, then the rWGS-system does make sense.

3.5 Comparison of the syngas routes

There are different aspects to consider when comparing the syngas production routes. Firstly, the energetic analysis with hard figures. Table 13 and Figure 25 show the energetic numbers. It is clear, that all processes are comparable in case of energy demand for a certain amount of syngas produced and that there are no substantial differences. Obviously, the solarthermal approach requires most of the energy in form of heat, provided by CSP, while the electrolysis pathways are fed mainly by electric power. It needs to be addressed, that the solarthermal approach produces waste heat at high temperature, which can be used to produce steam for instance. Since the simulation includes the DAC already, the heat cannot be used for this, unless additional CO2 should be captured for storage. The focus in this analysis should lie on the feasibility to integrate those technologies into an urban environment. The solarthermal approach could be an elegant solution, because the energy can be produced efficiently with the described CSP.





Figure 25: Comparison of the energy consumption of different syngas-production-routes at different ratios. The energy consumption is split into heat and electricity, where heat is delivered by CSP in case of the ST case and most likely by electricity or combustion in case of rWGS or SOEC.

ST: solarthermal; PEM+rWGS: proton-exchange-membrane-electrolysis and reverese water-gas-shift; SOEC: solid oxide electrolysis cell Co-electrolysis

The conversion to electricity by PV creates great losses, which is one reason why heat is the cheaper energy source than electricity. This is one of the reasons, why BiPV alone would probably be not enough to power a full conversion scheme. A direct solar energy generation would relieve the energy grid and decrease infrastructural cost. The downside is the relatively high area demand on the building and the required solar radiation. If a rooftop is shadowed by other buildings or is situated in colder climates, the power could possibly not be enough to fuel the process. Here, an energy or hydrogen grid is necessary, if the CO2 should be converted on site. The collection and transportation of the CO2 to a more centralized PtL-plant could be more reasonable in those scenarios. Another aspect of the syngas production on site is the need for high temperatures in all of the described technologies. This compromises the principle of an easy system, which can be implemented in urban scenarios without skilled workers. In theory, the high temperatures do not pose a problem, if suitable safety features could be installed. However, until this is adequately developed a syngas production in a more centralized and professional environment is preferable. Especially in comparison to the direct conversion, the high-temperature-processes pose more challenges to reach marketability. Overall, no technology is the absolute go-to-solution, but external factors could favour one over another.



3.6 Conclusion

The production of syngas using CO2 from DAC has been modeled and assessed for Solar TCC, PEM + rWGS and SOEC pathways. Additionally, three different H2:CO ratios have been analyzed for each of pathway. Results do not show relevant differences between the hydrogen to carbon monoxide ratios regardless of the chosen pathway. Nevertheless, two clear tendencies can be observed when comparing pathways: PEM + rWGS and SOEC strongly rely on electricity, while the energy input for the solar thermal approach is mostly heat. Although the total energy demand is lower for the electrolytical pathways, Solar TCC might be more efficient when considering the intrinsic energy losses of electricity production. However, the solar approach might not be feasible in certain geographical locations with poor solar radiation and its performance is still subjected to the sunlight intermittency. Last but not least, models forecast that LT-DAC should provide enough water from the air moisture to feed the process in all the scenarios.

Table 13: Simulation results for the syngas production routes.

		solarthe	ermal		PEM + r	WGS		SOEC		
H ₂ :CO Ratio		2,00	2,26	3,00	2,00	2,26	3,00	2,00	2,26	3,00
Electric duty	(kJ/molSG)	108	100	85	312	312	312	277	276	275
CO ₂ needed molH2O/mo	(ISG)	0,33	0,31	0,25	0,33	0,31	0,25	0,33	0,31	0,25
O ₂ obtained (molO2/mol	SG)					0,5				
Hot utilities (kJ/molSG)		402	402	400	59	42	39	88	83	71
Steam Gener (kJ/molSG)	ration	87	89	93	0,0	0,0	0,0	0,0	0,0	0,0
Cooling Wate (kJ/molSG)	er	7	7	7	4	5	3	0,0	0,0	0,0
Total Energy	GJ/t _{co2}	34	37	44	25	26	32	25	27	31
	MWh/t _{co2}	9,5	10,1	12,0	7,0	7,3	8,9	6,9	7,4	8,7

4 ENERGY SOURCE FOR A DECENTRALIZED URBAN SYSTEM

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4.1 Building-integrated photovoltaics as local electricity source for onsite DAC systems

Photovoltaics (PV) is one of the key technologies for a sustainable energy supply within a future, climate-neutral energy concept. By the direct conversion of sunlight into electricity, PV elements (solar modules) enable the energy generation without climate-damaging emissions. As proven technology, PV is used typically in large ground-mounted installations (MWp range) or on top of roofs (kWp range). The freely available areas for classic PV power plants are limited, because PV often compete here with other utilization claims, such as an agricultural use, human recreation or nature conservation. The integration of PV in urban areas, on the other hand, offers the possibility of "activating" a very large number of areas that are currently not used or are used far too little. Thus, building-integrated photovoltaics (BIPV) has the potential to up to 25% of the electricity consumption in Germany (Corti et al. 2020). This number can be reached by considering the entire building skin, and by this also overcoming the limitations of roof related competitions with other use cases like green roof concepts or necessary facility installations.

By integration, solar modules are becoming multifunctional building elements and, as roof or facade elements, as balcony parapets or shading aids, are enabling a wide range of design solutions for climate-neutral buildings. Beside the production of electricity, they take over additional functions within the building skin. The (local) removal of such an element leaves a functional or also only an aesthetic gap, which needs to be closed.

Integrated into differently oriented parts of the building envelope BIPV enables an electricity generation profile well balanced to the building-related consumption in the course of the day. In addition, due to a decentralized energy system with generation and consumption possible at the same place, grid-related aspects (e.g. costs and transportation losses) can be reduced significantly.

The local generation of electricity by BIPV is also of interest, if sustainable concepts for decentralized or semicentralized DAC solutions are developed, especially if such systems are directly connected to a building infrastructure. As explained in section 2.4.2, the different DAC approaches require different amounts of energy. In which way photovoltaic systems can deliver the necessary amount of electricity is discussed in the following.

4.1.1 Building-integrated photovoltaics potential of buildings

According to the project report of BIPVBoost (Corti et al. 2020) the technical potential of BIPV to cover the electricity demand in Germany is between 13% and 26% (depending on the selected scenario). Residential buildings have a capacity of 50 to 100 GWp of installed module power, generating about 40 to 85 TWh of electricity per year. In addition, non-residential buildings provide a capacity of about 30 to 60 GWp and an electricity generation of about 25 to 50 TWh per year.

The potential of an individual building strongly depends on its architectural design and the local situation. The most influencing properties are the location, the orientation, the shape, the used PV technology and the direct neighborhood influencing the amount of light irradiating the building skin. The later aspect is crucial, as the built and the grown environment can shadow solar modules in the course of the day and the year. Nevertheless, the opposite effect is possible too, as the albedo of the surroundings may have a positive influence.

To illustrate the dimension of electricity, which can be generated with a typical building, some examples are shown in Table 14. The values are simplified and neglecting possible shadowing effects of the environment.



As example, standard solar modules (330 W, crystalline silicon) or in case of vertical façade integration also thin-film modules (140W, CIGS) are used for this simulation. Location of all is Berlin.

It is important to consider, that the numbers for the generated electricity are the total amount per year. In the course of the day as well as over the seasons, the electricity is not generated continuously but varies strongly.

Type of building	Type of installation	Installed capacity [kWp]	Electricity generation [MWh/a]
Single-family house	Roof-top installation, standard modules, orientation southwest, 30 ° tilt 50 m ²	10	9
Multi-family house/	Roof-top installation, standard modules, flat-roof installation 800 m ²	144	119
factory building	Roof-top installation, standard modules, east/west installation (zick-zack, 15° tilt) 800 m ²	143	114
Office building,	Façade integration, standard modules, orientation south, 200 m ²	38	26
4 stories nign	Façade integration, design optimized colored thin-film modules, orientation south,200 m ²	24	16

Table 14: Exemplary data for the energy generaton potential of different building types.





Figure 26: Typical generation profile of a 10 kWp, south-oriented roof-top PV system with 30° tilt in the course of a day (blue: 1st of January, orange: 1st of July).

Figure 26 shows exemplarily a typical generation profile of a single-family house with a south-oriented rooftop installation. Two extreme cases, a real summer day and a real winter day, are shown. Two main aspects can be read out. Whereas in summer, the PV systems starts working already in the early morning and stops providing energy around 6 pm, in winter the generation is only between 8 am and 3 pm. As second aspect, atmospheric influences (e.g. clouds) cause short-term effects with temporary reduction of electricity generation. Therefore, for a PV system optimized to drive a local DAC system, a local battery system would be required. Non-critical would be the operation with grid connected systems (the common case), whereas the grid acts as a stabilizing system.

South oriented installations have their peak values at noontime, whereas other installations have different generation profiles. Depending on the user's behavior, installations with east/west orientation often provide a better balance of generation and consumption and possible battery storage systems can be optimized.

Façade-integrated solutions of PV are of interest more and more (example office building). In such situations, not necessarily the maximum yield is the most important aspect of the PV system but the architectural integration. Surface appearance and color can be key factors. In such cases, other PV technologies then standard silicon are often preferred. This results in the use of modules with lower power and finally the total amount of generated electricity is less than in a yield-optimized case.

4.1.2 Energy requirements of a Low-Temperature-DAC process

As explained in section 2.4.2, the total energy demand for a DAC process is the sum of electrical and thermal energy. Focusing on the LT-DAC, the amount of electricity is in the range of 200 to 300 kWh/t CO2. According to Viebahn et al. (Viebahn et al. 2019) the total amount of electricity needed to operate an entire LT-DAC process (example Climeworks), including fan, control, vacuum pumps, etc. is in the range of about 500 kWh/tCO2. Beyond that, the desorption process itself requires typically 1500 kWh/tCO2 of thermal energy.



Whereas the thermal energy e.g. from industrial waste heat or other sustainable heat sources can technically be provided continuously over a day, the electricity from a PV system (see Figure 26) is not available 24 h without temporary storage solutions. Depending on the season and on local (weather) conditions a PV system has a certain generation profile, which determines in principle the possible time window for operating a LT-DAC unit, if only the electricity, locally generated by PV, should be used. Therefore, an additional battery system to acts as temporary energy storage would be necessary to guarantee a continuous (24h) operation.

In a concept of integrating a DAC unit directly into the existing facilities of a building (e.g. exhaust infrastructure) the airflow through the DAC unit is driven by the existing fans. These fans are optimized for the building's requirements (airflow, pressure, continuous or varying operation) and do not fit perfectly to the stepwise process of absorption and regeneration. Therefore, additional valves and bypasses would be required, if DAC units are directly in line with the exhaust flow. In such situation, a set of small DAC standard units could be used with alternating operations enabling finally a continuous airflow.

In order to be independent of the local exhaust facilities, the alternative concept would use its own fan. Such operation would have less integration and with this, less synergetic effects but would be more independent of the building-given properties of the exhaust airflow. Assuming a battery or grid supported 24 h operation, a model DAC unit can be analyzed according to its energetic demands and the opportunities of a BIPV related energy supply. As example, values for the smallest standard unit DAC-01 of Climeworks are used in the following. Optimizing the absorption/desorption process with respect to the energy consumption and the maximum amount of absorbed CO2, a cycle time of 10 h can be obtained. This results in an electricity demand of about 50 kWh/d (1600 kWh/month or 19,2 MWh/a). (Heni 2020)

Heni also calculated the required size of a façade-integrated PV system (south orientation), which has to provide the required electricity demand of such a standard DAC-01 unit. Depending on the type of module, the area, a BIPV system would cover to fully support one DAC-01, is in the range of 540 to 1100 m2. The first value (crystalline silicon modules) would require building areas of about 20 x 30 m2. While such areas do not correspond to facades of individual residential buildings, such a facade is not unrealistic for industrial buildings. Similarly, thin film modules (CIGS or CdTe) require with an area demand of more than 1000 m² façade of at least 20 x 55 m2. Such areas could also be provided by large industrial buildings.

The calculations above considered the smallest known standard LT-DAC-01 unit with a daily capacity of absorbing 140 kg CO2 (Viebahn et al. 2019). In order to optimize the CO2 absorption process with respect to costs, area demand and maximum CO2 gain, the use of solar modules with best W/m2 ratio (highest efficiency) should be preferred.

4.2 Case study: Solar powered System

In order to assess the potential in closer detail, the whole production of synthetic fuels with a thermochemical cycle is assessed in a decentralized production unit powered by CSP. This approach follows the example of a technology demonstrated by ETH Zürich in which a parabolic solar dish with a solar reactor in the focal point is used as thermal energy source (Dähler et al. 2018). In the following figure, a conceptual flowsheet can be seen.





Figure 27: Process block diagram of the decentralized approach coupled with a solar parabolic dish. Image sources: IEA, 2014.

This unit would use CO2 from a building equipped with heating, ventilation and air conditioning system (HVAC). HVAC units are common in most of commercial and residential buildings across the world and as already mentioned, LT DAC units could be used to remove carbon dioxide from ventilation streams without a significant negative effect on the electric consumption used for building climatization. For this case study, the DAC-1 unit of Climeworks, with an average hourly CO2 output of 5.6 kg/h, has been considered (Viebahn et al. 2019).

This CO_2 will then be compressed, stored and converted into synthetic fuels in a smaller in-situ facility that would combine a TCC and FT synthesis process. The chosen parabolic dish is similar to the units installed in Maricopa, a solar electricity plant in the United States. Each of these devices can supply up to 48 kW of thermal energy (SolarPACES 2013). The assessment of the described case study is shown in the following table.

Several results from the previous table should be discussed. First of all, the carbon dioxide availability must be considered. As stated in section 2.5.5, the HVAC system of a large office building like the Fair Tower in Frankfurt am Main (Germany), could provide between 0.75 and 1.5 t CO2/h (Dittmeyer, 2019). The total surface occupied by the unit is estimated to be 1,185 m2: 105 m2 for the parabolic dish on the rooftop and 1,080 m2 of crystalline silicon PV panels on the façades to supply the 9.71 kW of electricity. A building similar to the Fair Tower, would have approximately 1,600 m2 of surface on the rooftop and a total of 36,480 m2 on the façades. Assuming that only 50 % of the rooftop is available and 25 % of the façade is suitable for installing PV-modules, the possible number of units installed is 7 (limited by the rooftop surface for this specific building shape). According to Table 6, these 7 dishes would be able to process 36.8 kg CO2/h, which is considerably below the CO2 that can be captured. Thus, it is safe to state that the CO2 supply will not be a constrain for the present decentralized approach.



Table 15: Results of the case study assessment. All the figures refer to design operation during daylight. ORC stands for organic Rankine cycle.

Parameter	Units	Value
Thermal solar power required	kWth	46.6
CO₂ input	kg/h	5.63
H₂O input	kg/h	-8.74
Net heat production (used in ORC)	kWth	-18.6
Net electric needs (considering ORC)	kWe	9.71
Fuel production	kg/h	1.65

Another parameter that must be discussed is the net heat production. Thanks to the performed heat integration, part of the heat is used for supplying other heat needs across the process. A remarkable consumer of this heat is the LT DAC. The remaining energy is used as an input for a micro organic Rankine cycle with an efficiency of 10 % (Rahbar, 2017) has been chosen due to its small scale. The combination of lower Rankine efficiencies and the LT DAC heat consumption leads to lower electricity production and thus, the need of an extra electricity input. Although the required electricity could be supplied by the grid, PV panels have been chosen to avoid adding stress to the existing electric infrastructure of the building and considering that the facility will be placed in Germany, where PV panels offer better performance than CSP for electricity production.

Overall, the present example shows a decentralized approach built with already available components that processes up to 5.63 kg CO2/h. This CO2 is further processed to 1.65 kg/h of FT product, which can be transformed to the desired liquid fuel in-situ or in a nearby refining facility. Thanks to the heliostat and the PV panels, no energy inputs from the energy grid are required. However, since grid integration is possible and even desirable in certain cases, potential strategies will be discussed in the following section.

4.3 Conclusion

One major obstacle in a future energy system for a country like Germany is the constant supply of enough renewable energy. The removal of CO2 from the air, which is required for a net zero economy, should therefore be as energy efficient as possible. Herein lies one of the benefits of a ventilation-integrated system. It utilizes synergies, for example by the dual-use of the fans for ventilation and DAC, which lowers the overall electricity consumption in comparison to separate systems. This integration also utilized otherwise unused space on the rooftop of buildings, as well as unused surfaces, e.g. facades. They have often potential to generate electricity by photovoltaics. Studies show, that such BiPV could at least partially power a DAC system, if complemented with an energy storage to flatten diurnal and seasonal variations. While the electric demand could be met, the heat demand is substantially higher. Concentrated solar power in form of a heliostat could provide some locally generated energy, but to exploit the whole capture potential of the ventilation system a grid integration instead of an island solution makes the most sense. This could come in the form of a constant supply with rather locally produced industrial waste heat or as integration into the national power grid. Latter would enable more buildings to be outfitted with a DAC unit, since a local potential for renewable energy is not mandatory in such a scenario. If coupled with an on-site P2X-conversion scheme, the energy demand rises further, mainly for the water splitting. The dynamic operation of the hydrogen generation could draw excess renewable energy from the grid and store it chemically in form of various hydrocarbons. In that way, the decentralized systems could provide stability and efficiency to the grid, by removing excess energy instead of shutting down the power source.



If the products can be converted back into energy, either by small power generators or by feeding them into secondary energy infrastructures, like the natural gas grid, the building integrated systems could be part of an energy storage solution, which is desperately needed to negate the variations common with renewable power sources.

Overall, decentralised and building integrated DAC- and P2X-conversion plants with local energy generation, could contribute to a future energy system, by providing negative emissions, a flexible energy sink and a potential energy storage, while exploiting synergies to further increase the efficiency.

5 FUEL SYNTHESIS

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5.1 Methanation

Production of synthetic or substitute natural gas is a well-known technology that has been deployed in areas where gas could not be naturally found or cost-effective feedstocks such as biomass or coal are available. There are several possible arrangements, but all of them require an effective refrigeration system due to the high exothermicity and the thermodynamic limitations at high temperatures of the methanation reaction (Heinz Hiller et al.)

The chosen flowsheet for the present study relies on 2 consecutive adiabatic fixed bed reactors with a partial hot recycle at the outlet of the first unit, although it is common to find up to 5 stages. The reactors are filled with nickel catalyst. According to literature, the operating conditions are between 250 and 700 °C and pressures above 20 bar. For the current simulation, outlet temperatures of 450 and 315 °C and pressures of 25 and 20 bar have been respectively chosen for the first and second reactors. Ideally, the fed syngas should have a 3:1 H2 to CO ratio. The outlet of the second reactor is assumed to be pure methane (Götz et al. 2016).

In order to store or distribute the produced fuel, water is condensed and removed and the SNG is compressed to 50 bar in a multistage compressor at the end of the process. The released heat across the process can be used to obtain high-pressure steam or in heat integration in other units upstream.



Figure 28: Layout of the methanation process. Energy streams have been removed for simplicity.





5.2 Methanol synthesis

Methanol production using synthetic gas as a raw material is normally performed in catalytic reactors at pressures between 50 and 100 bar, which are achieved in a multistage compressor, and temperatures from 200 to 300 °C. The reaction is exothermal and heat is normally removed through the refrigeration system of the reactor and a heat exchanger at the outlet. This waste heat can be used to produce steam or for heating other streams.

The conversion of syngas achieved per pass is normally 50 % due to thermodynamic limitations assuming that it is fed with a H2 to CO ratio of 2:1. In the separation part, non-reacted syngas is flashed and recycled (it can be injected between the stages of the compressor). Methanol is then distilled to the desired purity grade and stored or transported in liquid form (Ullmann, 2003).



Figure 29: Layout of the methanol synthesis process. Energy streams have been removed for simplicity.

5.3 Fischer-Tropsch-Synthesis

Fischer-Tropsch synthesis is a well-known process used for producing a wide choice of hydrocarbons from syngas. A range of pressures and temperatures can be found in the available literature depending on the feedstock and the desired final products. In the current study, the FT reactor is a fixed-bed reactor at 250 °C and 35 bar (Kaneko et al. 2000). Ideally, syngas should be fed with a H2 to CO ratio of 2.26:1.

The reaction yields to a range of carbon chains between C1 and C50 through an exothermal reaction pathway. The outlet must undergo a separation process to remove the lightest fraction (C1-C4), which can be reformed and recycled. There are several available reforming technologies such as steam methane reforming, partial oxidation or autothermal reforming. In the present study, autothermal reforming has been chosen because it does not require the supply of any additional heat (Ersöz 2008).

The model of the autothermal reforming reactor combines the endothermal dry steam reforming of hydrocarbons with exothermal partial combustion of methane. As a consequence, the reactor operates adiabatically. The oxygen required for the operation can be easily obtained from upstream processes such as electrolysis or carbon and water splitting. The selected conditions for the reactor are 900 °C and 40 bar and the expected conversion is 85 % (Heinz Hiller et al.; Ersöz 2008)

The heavier fraction can be purified and further refined in order to produce the desired type of fuel (e.g. diesel, kerosene, gasoline...). This upgrading process can take place in the facilities or in a traditional refinery nearby.





Figure 30: Layout of the FT process. The FT Products refers to a mixture of hydrocarbons between C5 and C50 that can be further processed and refined to obtain the desired fuel. Energy streams have been removed for simplicity.



Figure 31: Comparison of the energy demand per kg of final product.



5.4 Fuel processes comparison

Three models have been built in Aspen Plus, one for each fuel production process, to allow a brief comparison between them. It should be noted that, even though all the analyzed pathways use syngas as raw material, the optimal H2 to CO ratio differs between them. Thus, different H2 to CO ratios have been considered in the previous section.

Following the method of the solar syngas model, a heat integration in Aspen Energy Analyzer has been performed to calculate the optimal amount of utilities involved in the process. The results of these simulations per unit of syngas processed are shown in the table at the bottom of this section.

In the table, high temperature heat needs refer to those heat sources that must be at very high temperatures that, traditionally, rely on the combustion of fuels in furnaces. Although these requirements can also be supplied by CSP, the combustion of purges provide enough energy according to the simulations. As stated in the syngas production, a Rankine cycle would be a reasonable use of produced high and medium pressure steam.

It should be noted that the comparatively low molar output for the FT synthesis is caused by the production of a wide range of hydrocarbons between C5 and C50 with very high molecular weights. Another remarkable feature of Fischer-Tropsch synthesis is the production of more electricity than consumed as a consequence of the relatively moderate pressures needed, allowing the production of electricity in a turbine at the outlet of the syngas storage tank. The small oxygen input required by the FT synthesis is used in the autothermal reforming unit.

Table 16: Results of the fuel production models. The required energy and raw materials for each fuel is shown. The heading "CH4" stands for methanation process, "CH3OH" for methanol synthesis and "FT" for Fischer-Tropsch synthesis. "HPS" and "MPS" mean high-pressure steam and medium pressure steam respectively, while "FP" stands for final product.

Parameter	Units	CH4	CH₃OH	FT
High temperature heat	Mio. EUR 2016	0	0.424	1.16
(T > 900 °C)	kJ / mol SG	51.9	32.8	72.2
HPS & MPS produced	kJ / mol SG	0.558	1.379	-0.364
Electricity required for compressors	kJ / mol SG	10.2	11.0	8.0
Cooling water	kJ / mol SG	0	0	0.0392
Oxygen input	mol O2 / mol SG	0.250	0	0.359
Water obtained	mol H2O / mol SG	0.250	0.333	0.0250
Final product produced	mol FP / mol SG	0.250	0.333	0.0250

Table 17: Metrics to compare the Fuel synthesis to other processes.

Fuel	Methane	Methanol	FT
Specific electricity needed (MJ/kg $_{\rm FP}$)	27	10	21
Specific heat needed (MJ/kg _{FP})	100	38	101
Specific total energy needed (MJ/kg $_{\rm FP}$)	127	47	123
Specific CO ₂ capture (kg _{CO2} /kg _{FP})	3,66	1,26	2,77
Specific total energy needed (GJ/ $t_{_{CO2}}$)	35	37	44
Energy Efficiency kJ _{HHV} /kJ	0,44	0,48	0,39

5.5 Conclusion

The production of different fuels from syngas was compared, namely methane, methanol and Fischer-Tropsch product. On the one hand, the models indicated that methanol synthesis is the pathway that generates lowest waste heat and shows the best yield per mol of syngas, but it also requires the highest electricity inputs per mol for compression purposes. In addition, its energy content (HHV) is considerably inferior, which explains the lower energy demand per mass of final product. On the other hand, Fischer-Tropsch is the only process that produces more electricity than it consumes, even though an oxygen input is required for the reforming of the hydrocarbon fraction below C5. While it can be safely stated that methanol and FT synthesis outputs are easier to store and transport due to higher energy densities, methanation should not be dismissed since it can be a valuable option given the already available natural gas infrastructure.



6 ELECTROCHEMICAL CONVERSION OF CO₂

Matthew Mayer

Electrochemical (EC) conversion of CO¬2 is an emerging technology for directly upgrading CO2 to valuable products in a single reactor, which operates with inputs of just electricity, water, and a CO2 supply. This approach could be an attractive alternative to conventional heterogeneous catalytic routes since it can be accomplished at near-ambient temperature and pressure, and could therefore be more versatile for use in distributed applications such as in urban scenarios. This would also bypass the need for generation and handling of H2, instead achieving hydrogenation electrochemically. However, EC CO2 conversion is at an earlier stage of development compared to traditional routes, and thus the configuration and operation parameters of such reactors are presently poorly defined. There exist a number of scientific and engineering challenges which must be overcome for this technology to reach feasibility (Norskøv, J., Latimer, A., & Dickens, C. 2019). Nevertheless, progress in this field has advanced considerably over recent years.

The heart of an electrochemical CO2 conversion device is the electrochemical cell. This includes a cathode where electrons are delivered to CO2 for reduction transformations into various products, an anode where electrons are extracted by the oxidation of water to generate O2, and a separator to physically and electronically separate the electrodes from each other while conducting ions between them (Figure 32a). There are a few distinct technological approaches to electrochemical CO2 electrolysis (CO2E), classified herein as low-temperature (LT) and high-temperature (HT) (Küngas 2020). HT-CO2E includes solid oxide and molten carbonate electrolysis, which typically operate at temperatures over 600 °C, while LT-CO2E involves CO2 conversion from aqueous solutions, using polymer membranes and operating at temperatures below 100 °C. HT electrolysers have achieved higher TRL, but LT have characteristics, which make them attractive for use in distributed or urban applications (discussed in section 2.6).

LT-CO2E systems will therefore be the focus of this report. While specific device designs are still under development, to date the prototypes generally resemble water electrolysis devices (PEM or alkaline electrolysis). As shown in Figure 32a, such cells typically use an aqueous medium and membrane separator to conduct ions between anode and cathode.



Figure 32: Electrochemical CO₂ conversion. a) Diagram of a single cell for alkaline CO₂E composed of an anode evolving O2, a membrane separator (dashed line), and a gas diffusion cathode converting CO₂ to multiple products (Burdyny, 2019). b) Schematic of a multi-layer CO₂ electrolyzer stack composed of multiple anode/membrane/cathode cell units (Endrődi, 2019).

Achieving practical rates (electrochemical current densities) requires overcoming the low solubility of CO2 in water, and thus gas diffusion electrodes are employed, which enable direct feeding of gas-phase CO2 to the porous catalyst surface (Burdyny und Smith 2019). Similar to the case for water electrolysers, these individual CO2E cells can be combined into larger multi-cell stacks.


A primary challenge in EC CO2 conversion is reaction selectivity, since multiple different products are usually formed, often as a mixture. In LT-CO2E upwards of 16 different products have been observed, including carbon monoxide, formic acid, methane, ethylene, ethanol, and propanol (Kuhl et al. 2012). In aqueous LT systems, the electrolysis of water to generate H2 is a competitive side-reaction. Among the different possible products, various numbers of electrons and CO2 molecules are required, and the products occur in liquid or gas phases. Selectively producing just one desired product is key for viability, since chemical separations are costly (Greenblatt et al. 2018). The research field is thus largely focused on addressing the selectivity challenge by research and development on catalyst materials and reactor designs.

For distributed applications such as DAC in buildings coupled with on-site EC conversion (discussed below in section 6.5), the target products should be chosen primarily based on their usefulness and value for distributed on-site production (e.g. fuels) and the ability to safely generate and store them within urban environments. This latter point means that hazardous products like carbon monoxide should be avoided, and in general, that liquid (or easily liquefiable) products are preferred since they are easier and safer to store locally and to transport, as compared to gaseous products. Candidate products would therefore include organic acids (namely formic acid) and alcohols (methanol, ethanol, propanol). With development of direct formic acid fuel cells and direct alcohol fuel cells, these products could be used as fuels, making distributed refueling stations a possibility. To date, the simple two-electron products formic acid and carbon monoxide are the only products toward which both high current densities (>100 mA/cm²) and high faradaic efficiency (>90%) have been simultaneously achieved, although there has been recent progress toward production of 12-electron products ethylene and ethanol (Luna et al. 2019). Continued development of catalysts and reactors targeted at generating these multi-carbon liquid products is expected to yield further advances toward the goal of direct LT-CO2E synthesis of liquid fuels.

6.1 Technology Readyness Level

Electrochemical CO2 reduction has been widely studied for decades but LT-CO2E is still in the laboratory stage (TRL ~4), with research and development toward improving product selectivity, conversion rate, and stability. Several companies have initiated commercial efforts on CO2E. These mostly include CO2 conversion to CO, since high CO selectivities have been achieved, and CO currently presents the most attractive business case based on techno-economic analyses (Bushuyev et al. 2018; Jouny et al. 2018). In particular, HT solid oxide electrolysis technologies have had success toward commercialization (Sunfire GmbH, Haldor Topsøe). A few companies are advancing aqueous LT CO2E, including Opus12, Dioxide Materials, Avantium, Siemens, and Prometheus. Several of these claim progress in forming multi-carbon and liquid products at commercial scales, but few details about these capabilities are public at this time.



Table 18: Comparison of EC CO₂ conversion products in terms of estimated energy and cost.

* Assumed operating voltage 3 V and perfect faradaic efficiency to specific product.

 $^{\rm b}$ assuming 1 t/hCO_2 capture and complete conversion to product.

° from (Jouny et al. 2018) and references therein.

		formic acid HCOOH	ethanol CH ₃ CH ₂ OH	propanol CH ₃ CH ₂ CH ₂ OH
e-, CO ₂ per product molecule		2 e-, 1 CO ₂	12 e-, 2 CO ₂	18 e-, 3 CO ₂
Electrical energy input ^a	kWh/tCO₂	3655	10964	10964
	kWh/t ^{Product}	3496	20975	24081
Energy excess (heat)ª	kWh/tCO ₂	2132	6798	7236
Daily product generation ^b	t/day	25.1	12.5	10.9
Product market price [°]	USD/t	740	1000	1430
Annual global production [°]	Mt	0.6	77.0	0.2
CO ₂ electrolyzer power ^{a,b}	MW	3.65	11.0	11.0
Energetic eficcience	kJHHV/kJElec	0,45	0,39	0,39

The TRL for production of CO by HT-CO₂E is at approximately 7-8 with the accomplishments of some of the companies above (Küngas 2020). But for production of other products the TRL level is mainly <5. Current research largely focuses on the design of new electrocatalyst materials and reactor concepts for improving selectivity toward a single target product. More practical challenges are starting to receive increased attention from researchers, including stability, energy efficiency, CO_2 utilization efficiency, and conversion rate. Based on the similarity of LT aqueous CO_2E cells to those used in PEM or alkaline water electrolysis, it is expected that the experience from the electrolysis sector will benefit the advancement of this field. Additional challenges exist in the management of chemical products (liquids and gases) which will be more technically challenging than H2 collection from electrolysis.



6.2 Energy Demand

Since the design and operational parameters for an LT CO2E system are not standardized, our initial analyses will use performance characteristics taken from the laboratory and from literature reports, along with multiple assumptions regarding efficiency. Although practical devices will certainly require auxiliary equipment such as pumps, valves, etc., the dominant energy demand for EC is the electrical power input needed to drive the reactions within the cell. In the analysis below, we estimate and compare this electrical energy requirement toward the production of several possible products.

In Table 18, we present an analysis of three potential EC CO2 conversion liquid products. Considering simply the number of electrons and CO2 molecules needed to form each product molecule, and the estimated voltages required to drive the cell, we calculate the electrical energy needed to convert 1 metric ton of CO2 into product.

Electricity demand is a key factor differentiating the possible products, with the simpler two-electron products like formic acid (and carbon monoxide, not shown) requiring less electricity due to their requirement of only two electrons per molecule. Further reduced products require many more electrons, which directly increases the electricity demand per molecule of CO2 converted. But this also results in more energy density stored in the product, giving the more reduced multi-carbon alcohols progressively higher value as fuel.

Efficiency losses arise due to over-voltages required to drive the challenging multi-electron reactions at both electrodes, plus the transport resistances imparted by the membrane. These losses produce heat which could conceivably be coupled to help supply the thermal demand of DAC unit CO2 desorption process. Efficiency improvements can be expected with further development of electrocatalyst materials and reactor designs.

6.3 Cost

Since detailed considerations of reactors and balance of system would be very speculative at this point, a system-level cost estimate is not conducted at this stage. Furthermore, the operation costs of CO2E are highly sensitive to electricity costs, and can thus vary greatly depending on the location. The electricity cost is dictated by the number of electrons needed per product, the electron-to-product conversion efficiency (faradaic efficiency), and the operational voltage needed to drive the reactions at practical rates. Products requiring fewer electrons tend to require less voltage, so electricity costs per ton of CO2 converted are considerably lower when targeting two-electron products.

While detailed costs will not be speculated on here, several recent techno-economic analyses provide useful insight toward practical implementation of LT CO2E – see (Bushuyev et al. 2018; Luna et al. 2019; Jouny et al. 2018; Spurgeon und Kumar 2018). These studies show that the levelized cost of products are strongly influenced by performance characteristics of the CO2 electrolyzer (current density, faradaic efficiency, electrode material cost).

6.4 Operational parameters

Sizing: An EC CO2 reactor comprised of multiple individual cells operating in a stacked configuration (like a water electroyzer) can readily be sized for the desired application. In the case of operating on-site and coupled to a CO2 source (such as building integrated DAC, discussed below) which delivers a certain daily/hourly flux of CO2, the size and number of EC cells can be customized to achieve the desired rate of CO2 conversion. The total required electrode surface area is a function of the target product, the operational current density, and the targeted rate of CO2 feed conversion.



Intermittent operation: Since LT CO2E reactors operate near ambient temperature and pressure; they can potentially be operated intermittently. This could be important when their operation is coupled to an intermittent supply of CO2 (such as from DAC) and when powered by intermittent electricity (such as from PV).

Auxiliary components: Liquid pumps, blowers, condensers, compressors, and power control units are expected to be key auxiliary components, although a detailed system-wide study for LT CO2E has not yet been reported in the literature.

6.5 Urban integration concept – DAC coupled to LT CO₂E

Distributed DAC of CO2 could be paired with on-site conversion by low-temperature electrochemical reactors, providing several conceivable advantages. LT CO2E operates at near-ambient pressure and temperature (in contrast to many conventional catalysis technologies), so it might be coupled directly with DAC units without the need for intermediate gas storage, heating, or compression infrastructure. This would also avoid the need for co-generation of hydrogen, which is required for other approaches to CO2 hydrogenation. Water vapor produced by the DAC process can also supply the electrolyser with necessary pure water.

CO₂ electrolysis typically runs in continuous flow mode, which could allow integration with a continuous CO2 source such as a network of DAC modules running under staggered adsorption/desorption cycles.

Waste heat is generated by CO2 electrolysis, deriving from kinetic overpotentials and Joule heating. An estimate of the magnitude of energy excess in LT CO2E is provided in Table 18 It is derived from relating the operation voltage of typical state-of-the-art reactors (about 3V) and the standard reaction voltage based on free energy values for the different products. On the basis of excess energy per ton of CO2 converted, it can be seen that the electrolyser could conceivably produce waste heat at magnitudes similar to the heat demand of the DAC units (compare section 2.4.2). Reactions requiring more electrons per CO2 molecule (e.g. to form alcohols) will generate more waste heat per CO2 converted. However, LT CO2 electrolysers produce low-grade heat, likely unable to generate temperatures >100 °C unless advanced pressurized cells are developed. Further efficiency gains in CO2E systems will lead to decreasing waste heat production. Nevertheless, this analysis shows that the CO2E waste heat and DAC heat demand are of similar magnitude and thus may present opportunities for synergetic integration.



7 ENHANCING SYNTHETIC FUEL PRODUCTION USING MEMBRANE REACTORS

Homa Hamedimastanabad, Torsten Brinkmann

7.1 Introduction

The entire cycle of the carbon capture and utilization process cannot be consummated, unless the captured CO2 consolidates itself as the major building blocks for production of diverse high-demand CO2-based fuels and chemicals. Figure 33 shows the most prominent future candidates for large-scale CO2 utilization routes via thermocatalytic conversion. CO2 and renewable H₂ can be directly used to produce methane, methanol and liquid hydrocarbon transportation fuels (LHTF), like gasoline, kerosene and diesel. Moreover, methanol is clearly identified as a pivotal intermediate for production of manifold chemicals (dimethyl ether, formaldehyde, formic acid, lower olefins, acetic acid and higher alcohols), and LHTFs via the so-called methanol-to-gasoline (MTG) and Mobils-olefins-to-gasoline-and distillate technologies, instead of the traditional Fischer-Tropsch (FT) synthesis approach. Nonetheless, several of these transformations (methanol synthesis from CO2 or syngas, methanation, syngas production, FT reaction, and dimethyl ether synthesis) are limited by equilibrium conversion and suffer from high amount of water production, which causes catalyst sintering, or thermal deactivation. The in-situ removal of the water from the reaction system not only mitigates the two aforesaid problems, but also intensifies the reaction rate, and offers a unique opportunity to merge reaction and separation in one single piece of equipment with potential savings in both CAPEX and OPEX. This tactic can be carried out through the incorporation of membrane technology into the reaction system. Here in, we demonstrate the proof of the aforementioned concept for methanol synthesis via direct CO2 hydrogenation using process simulation tools. While an analogous study can be carried out for the other routes, we chose the methanol synthesis route for this purpose due to two reasons: 1: methanol seems the most promising green fuel for the near-term future, which is in pursuant to the prompt measures required to meet the Net Zero commitments by 2050, as explained in the following paragraphs. 2: methanolation has a much lower conversion compared to the other routes. Synthetic methane, with a high TRL of 7 and its already existing pipeline infrastructure for storage and distribution as well as milder operating pressure, might be a promising nominee for the future energy carrier; however, currently, it is less attractive than methanol due to its far lower market price and energy density. Moreover, given the several operating Gas-To-Liquid plants worldwide, F-T technologies are of high maturity with a TRL of 9; however, these facilities are operating based on syngas from non-renewable feedstocks (natural gas and coal). Nonetheless, the upstream CO2-based syngas production is currently not a mature technology, earning a TRL of 6 (Jarvis und Samsatli 2018; Chauvy et al. 2019; Garcia-Garcia et al. 2021). In contrast, the methanolation process via the direct CO2 hydrogenation, with the TRL of 8-9, is of high potential for commercialization in three to five years. The global demand of this alcohol was reported 99 Mt in 2020, which is among the highest in the chemical sector. Based on the premises, green methanol has all the potential to shortly emerge as one of the key pieces of the carbon cycle puzzle, notwithstanding this fuel, among others, is not yet economically viable for production due to the current high costs of hydrogen synthesis and carbon capture.





Figure 33: Carbon utilization pathways via thermocatalytic conversion with operating conditions and TRLs (blurred to sharp fonts denote low to high TRLs)

The basic idea of green-methanol-based e-fuel hubs was first suggested by Nobel laureate George Andrew Olah in 1994, known as the "methanol economy". At that time, the primary goal of the scheme was not carbon reduction, but hydrocarbon replacement with synthetic fuels. However, it has been lately realized as a promising sustainable energy framework for the future carbon-neutral world, where green methanol is produced and stored in renewable energy prone areas (known as methanol-based e-fuel hubs) for either further processing to other commodities, or the direct shipment to the market. Methanol synthesis is a set of reversible reactions, which can be represented by the following equations:

$$CO(g) + 2H2(g) \rightleftharpoons CH_3OH(I)$$
 $\Delta H_{298K} = -128 \frac{KJ}{mol}$ Eq. 1

. .

$$CO_2(g) + H2(g) \rightleftharpoons CO(g) + H_2O(g)$$
 $\Delta H_{298K} = +41,19 \frac{kJ}{mol}$ Eq. 2

$$CO_2(g) + 3H2(g) \rightleftharpoons CH_3OH(I) + H_2O(g)$$
 $\Delta H_{298K} = -49,51 \frac{kJ}{mol}$ Eq. 3

Methanol is typically derived from fossil-fuel-based syngas (CO, H₂ and CO2); however, the mixture of carbon dioxide, presumably from carbon sequestering sources, and hydrogen can be an alternative feed for methanol plants. The derivation of methanol from the latter has been studied in several publications based on experiments as well as simulations. The reactions take place over the commercial state-of-the-art catalyst Cu/ZnO/Al2O3. The industrial operating conditions are 483.15-543.15 K and 5000-10000 kPa (Van-Dal und Bouallou 2013).



Different membrane designs and prototypes are proposed and studied by several publications (Gallucci et al. 2004; GALLUCCI und BASILE 2007; Atsonios et al. 2016; Leonzio 2018; Raso et al. 2021). In this report, we present a rigorous model of an MR by eliminating the common assumptions in the literature. The model requires no analytical correlations for thermodynamic and transport properties, which often fail to reflect the system behavior accurately. An equation-oriented simulator, Aspen Custom Modeler, is employed to solve the problem while obtaining accurate physical properties. This model will be used to simulate methanol production in order to determine for which heat transfer modes and process conditions the installation of an MR is more impactful. For this, we evaluate the conversion and selectivity of the methanol reaction for two different reactor geometries (Section 7.4.1). We also propose the appropriate sweep gas stream and further investigate the effect thereof on the two metrics (Section 7.4.2). Due to an automated exportation facility compatible to commercial process simulators such as Aspen HYSYS or Aspen Plus, the proposed MR module can readily be embedded and exploited within a standard flowsheet for further energy analysis at the flowsheet level (Section 7.5).



7.2 Methodology

Figure 34: Membrane reactor module schematics with cross-sectional views a) adiabatic and b) non-adiabatic

In this section, two generalized MR models for a fixed-bed heterogeneous gas-phase reactor are proposed. The schematics of tubular MRs for both adiabatic and non-adiabatic heat transfer modes are depicted in Figure 1. The reaction takes place on the retentate (reaction) side, whereas the permeate side is intended to in situ withdraw one or more products from the reaction environment. To acquire a better understanding of the internal structures, the cross-sectional view of each reactor is also provided on the right hand side of each module. In order to develop rigorous models for both configurations, the differential equations which describe material and energy balances of each system and the corresponding kinetics' equations should be coupled and solved



simultaneously. The modeling description (Hamedi und Brinkmann 2021) is not covered here as it does not lie in the scope of this report. In this study, we employed the equation oriented process simulator Aspen Custom Modeler (ACM) V11 to solve the equation set. For this highly non-linear problem, the standard mode with the variable and equation convergence criterion was applied. The Redlich-Kwong-Soave equation of state with modified Huron-Vidal mixing rules (RKSMHV2) was used to predict the thermodynamic properties. The fluid property package file was created in Aspen Plus V11 and configured in ACM. The transport properties such as viscosities and thermal conductivities are also calculated using Aspen Properties. We used the kinetics model which is rearranged by Van-Dal et al. (2013).

7.3 Design data and specifications

The zeolite-based hydroxyl sodalite membrane (HSOD) is a promising membrane for methanol production application due to the high selectivity of H2O/H2. Furthermore, water removal can improve catalyst lifetime, since its presence leads to catalyst deactivation via sintering. For this study, we assume a defect-free HSOD with 100% of water selectivity and the highest H2O permeance, which is reported in the literature (Khajavi et al. 2009; Rahimpour et al. 2011; El Sibai et al. 2017), i.e. 10-6 kmol/(s m2 kPa). It is worth mentioning that due to the customizable simulation platform used in this study, any theoretical or empirical models for species' permeances can be incorporated into the governing equations. Hence, it is envisaged to assess the application of other membrane materials including high temperature stable polymers. The other specifications that form the basis for the result section are listed in Table 19.

Table 19: Design data and specifications

Furthermore, the membrane reactor volume (MRV), which is defined in Eq. 4, is considered a constant value for both reactor geometries presented in Figure 34 In other words, we consistently use a diameter of 0.6 m for the outer shell of the adiabatic reactor regardless of membrane tube numbers. However, for non-adiabatic MRs, reactor diameter should be adjusted according to the number of reactor tubes. Note that for this type of geometry, the number of membrane tubes and reactor tubes are equal. Therefore, for the non-adiabatic design, is set at 0.1897, 0.1342, 0.1095, 0.08485, 0.0949 and 0.0775 m for 10, 20, 30, 40, 50 and 60 tube numbers, respectively. For non-adiabatic CRs, the membrane diameter approaches zero.

MRV=Reactor Volume+Membrane Volume Eq. 3

7.4 Methanol Conversion Enhancement

7.4.1 Membrane reactor performance without sweep gas

7.4.1.1 Adiabatic membrane reactor

Figure 35 demonstrates membrane's effect on conversion and selectivity of an adiabatic system (Figure 34a) for different operating pressures, 2000, 5000 and 7500 kPa. A reactor with membrane tube number equal to zero corresponds to a CR. As shown, both conversion and selectivity of the reaction system increase with pressure. This is because higher pressures shift the equilibrium of the methanol reaction (Eq.3) towards the product side, which has a fewer number of moles. On the contrary, pressure variations do not have any impact on the reverse water gas shift reaction (RWGSR), Eq. 2, which has an equal number of moles in both sides.



As can be seen, at 7500 kPa, the CO2-to-methanol conversion improves by 70.0% from 15.3% to 26.1% as the number of the membrane tubes increases from zero to 60. However, the selectivity drops by 16.3% from 56.4% to 47.2%. A similar trend can be observed at 5000 kPa, with a 52.8% increase in conversion and an 8.3% reduction in selectivity. The steep declines in the selectivity can be explained as follows. Due to the high exothermicity of the methanol reaction, the temperature along the reactor monotonically increases and this favors the RWGSR, which is endothermic. In other words, selectivity decreases at higher temperatures. The water removal in MRs even amplifies the temperature increase, which leads to declines in the selectivities.

Both conversion and selectivity slightly decrease for the case of 2000 kPa. This is attributed to the low driving force across the membrane and, in turn, minimal water removals. Nevertheless, even the very limited expectations for conversion improvement, due to the limited product removal, is offset by the loss of reactor volume as the membrane tube number increases.



Figure 35: Adiabatic reactor's performance for CR and MR a) CO₂-to-methnol conversion b) Methanol selectivity (Fig3)

7.4.1.2 Non-adiabatic membrane reactor

The differences in performance of CR (solid lines) and MR (dashed lines) for a non-adiabatic reactor (Figure 34b), which is cooled down by a high amount of cooling water, are shown in Figure 4. Note that in non-adiabatic configuration, CR is composed of different numbers of tubular reactors with no membrane tubes in the core. Since the MRV and reactor volume are equal and constant for CR scenarios, and the cooling water flow-rate is set at a high value, the conversion does not change significantly with increasing reactor numbers. However, the selectivity slightly increases with the reactor tube number. This is because the RWGSR is inhibited when the reactor is kept at lower temperatures. As mentioned earlier, higher pressures favour both conversion and selectivity of both CR and MR.

As shown in the figure, at higher pressures of 5000 and 7500 kPa, an MR outperforms its corresponding CR in terms of conversion with only a slight decrease in selectivity. In contrast, no significant improvements can be observed between CR and MR at 2000 kPa.

At the pressure of 7500 kPa and 60 reactor tubes, the conversion can be improved by 96.2%, from 21.1% to 41.4%, compared to the corresponding CR. This enhancement is associated with only a 4.9% reduction in selectivity. In comparison, the MR with the operating pressure of 5000 kPa and 60 reactor tubes shows a 52.7% gain in conversion with a 5.7% decline in selectivity.



As expected, higher conversion values can be achieved in non-adiabatic reactors, both CRs and MRs, as compared to the adiabatic counterparts. However, the membrane installation for the non-adiabatic configuration is more impactful than for adiabatic reactors, especially at higher pressures. This is because non-adiabatic MRs has higher conversion changes, 96.2% at 7500 kPa, as compared to adiabatic one with a 70.0% increase at the same operating pressure. More importantly, in non-adiabatic MRs, selectivity decreases only by 4.9% versus 16.3% in adiabatic schemes. A similar conclusion about selectivity can be deduced for the operating pressure of 5000 kPa.



Figure 36: Non-adiabatic reactor's performance for CR and MR a) CO₂-to-methnol conversion b) Methanol selectivity (Fig4)

7.4.2 The effect of sweep gas use on membrane reactor performance

In this section, we study the impact of sweep gas use on MRs' performance. For this purpose, we suggest the hydrogen feed as a candidate for the sweep gas stream. In fact, a portion of the inlet hydrogen enters membrane conduits before compression in order to counter-currently sweep the permeation side with respect to the gas flow in the reaction side. Here, we assume the hydrogen feed at atmospheric pressure. The basic idea of the proposed design for an adiabatic reactor is presented in Figure 37. An analogous process design can be illustrated for the non-adiabatic scenario when the adiabatic reactor is substituted with the non-adiabatic counterpart. The employment of hydrogen as sweep gas offers several advantages: it can increase the water permeation flux without loss in the reactor volume as compared to adding more membrane tubes, it decreases H2 permeation for a non-ideal membrane, and it only imposes a very limited additional power utility to compensate the pressure drops in membrane tubes, HEX-102 and KD-101.

Figure 38 and Figure 39 reveal the impact of the hydrogen sweep gas use on the performance of the adiabatic and non-adiabatic MRs, respectively. As shown in the figures, in both configurations, the sweep gas introduction becomes more effective as the membrane tube quantity increases. Regardless of the operating pressure and heat transfer modes, the conversion reaches a plateau after experiencing improvements with the hydrogen flowrate increase. For an adiabatic MR with 60 membrane tubes and the highest rate of sweep gas (100 kmol/h), the conversion increases by 19.3%, 29.8% and 69.8% at 7500, 5000 and 2000 kPa, respectively.



The reaction conversion enhancements are accompanied by only slight decreases in selectivity for higher pressures of 5000 and 7500 kPa and even a selectivity improvement at the pressure of 2000 kPa. Similar behavior can be realized for the non-adiabatic geometry. The conversion of an MR with 60 membrane tubes rises by 15.7%, 30.2% and 55.5% at 7500, 5000 and 2000 kPa, respectively. At the same time, the selectivity only slightly declines for 7500 and 5000 kPa, and increases by 5.4%, from 40.5 to 42.7%, at 2000 kPa.

It should be noted when the operating pressure is at 2000 kPa, the water penetrates through the membrane from the permeation to the reaction side in the beginning of both adiabatic and non-adiabatic MRs. This undesirable phenomenon can be counteracted by increasing the sweep gas flowrate.



Figure 37: Membrane reactor configuration with H2 as sweep gas



Figure 38: The impact of H2 sweep gas on adiabatic MRs' performance a) CO₂-to-methanol conversion b) Methanol selectivity





Figure 39: The impact of H2 sweep gas on non-adiabatic MRs' performance a) CO₂-to-methanol conversion b) Methanol selectivity

7.5 Energy and exergy analysis

In this section, the proposed membrane reactor model will be embedded within a methanol process flowsheet, which is developed in Aspen HYSYS V11. This holistic integrated framework enables us to accurately probe the role of an ideal membrane reactor in the performance of an entire methanol process flowsheet, and analyze to what extent the employment of this technology impacts reaction conversion and, more importantly, the overall utility demands of the plant. Figure 8 presents the process flowsheet diagram of a methanol production plant, which is aided with a water-selective membrane reactor. The plant is fed by pure CO2 and H2, which is generated by water electrolysis using renewable energy sources. The feeds are assumed at near atmospheric conditions (130 kPa and 308.15K). The feed is mixed with the recycle stream after compressed to pressure of 5000-10000 kPa in a 4-stage compressor (K-101) with interstage cooling. The mixture is heated to temperature of higher than 483.15K in HEX-101 and then routed to the water-selective membrane reactor (MR-101). The reactor product stream is cooled to 308.15K using cooling water. The non-reacted gases are separated from condensable products, methanol and water, in a knock-out drum (KD-101) and then recycled to the reactor inlet. The liquid product, crude methanol, is expanded in a valve to 130 kPa, and sent to the second separator (KD-102) to recover and further recycle the residual gases, which contains mostly CO2. The mixture of water and methanol is preheated and enters the distillation column T-101 to reach to the product purification of 99% for both methanol and water. A very limited amount of CO2, along with other possible non-condensable impurities, is drawn from the column condenser as shown in the figure. The permeate stream coming from MR-101 is sent to HEX-101 and then KD-103 to remove the produced water and recycle any gases penetrating through the membrane. In case of ideal water selective membrane, K-103 is not necessary.

The process was simulated using Aspen HYSYS V11. The MR model, which is developed in Section 2, is converted to a HYSYS package model and employed as an ACM operation unit in the process flowsheet. "Dominate Eigenvalue" is used as the acceleration method for the single recycle unit before HEX-101.





Figure 40: Process flow diagram for a methanol production plant aided with a water-selective membrane reactor

At the operating pressure of 7500 kPa and isothermal condition, where the membrane reactor recruitment is more advantageous, the power requirement of the conversion and separation process (excluding the feed compression) is 13 kWh/tCO2 for the MR-based process compared to 20 kWh/tCO2 for a CR-based process. In addition, the power needed for feed compression from 130 to 7500 kPa is about 410 kWh/tCO2, which dominates the overall process power requirement for both CR- and MR-based cases. However, it should be considered that the feed compression power requirement is dependent on the inlet pressure, which is here assumed at near atmospheric pressure for both CO2 and H2. Nevertheless, the storage pressure of the raw materials can be up to 10000-30000 kPa. In the latter scenario, the power demand for feed compression should not be any concern. Otherwise, the elevated power demand for the feed compression may call for high performance catalysts operating at milder operating pressure. Furthermore, given that the produced water can partly be separated from methanol inside the membrane reactor, it is also possible to reduce the heating load of the distillation column (T-101). This corresponds to a 10 % thermal exergy saving. An MR-based process can reduce (or in non-sharp separation remove) the size of the distillation column (T-101) since the separation can be partly (or completely) carried in the membrane reactor. This especially offers an advantage of smaller footprint for decentralized DAC systems.

7.6 Material balance analysis for the Urban System

The methanol production plant consumes about 1.375 tCO2/tMeOHand0.1875 tH2/tMeOHas the raw materials. Considering the urban system scenario's capacity of 0.75-1.5 tCO2/h, 0.54-1.1 tMeOH/h as the final product is producible. This corresponds to the demand of 0.10-0.21 tH2/h.



7.7 Conclusion

In order to show the primary potentials of MRs' application in synthetic fuel process intensification, we developed a generalized MR model and later employed it for CO2 hydrogenation to produce synthetic methanol. We evaluated the impact of MR employment on reaction conversion and selectivity. The outcomes indicate that for higher operating pressures, the MR employment can boost the reaction conversion by up to 70.0% and 96.2% in the adiabatic and non-adiabatic heat transfer modes, respectively. This results in a 16.3% reduction in reaction selectivity in an adiabatic and only 4.9% in a non-adiabatic system. This implies that MRs are more impactful on the performance of the non-adiabatic design. We also used a portion of the H2 feed as a sweep gas and studied the effect on the MR's performance. According to the results, the sweep gas recruitment is more helpful when used in an MR with a higher number of membrane tubes. In this scheme, for adiabatic MRs, the conversion can be enhanced by up to 69.8% at 2000 kPa and 19.3% at 7500 kPa. In contrast, the values reduce to 55.5 % at 2000 kPa and 15.7% at 7500 kPa for non-adiabatic design. However, in this configuration, the reaction selectivity increases at lower pressures and only slightly decreases at higher pressures. While the proposed MR module is used to describe the primary potentials of MRs' application for methanol synthesis, it is capable of accommodating other theoretical or empirical equations for system characterization and being employed as a built-in operation unit in host applications, such as Aspen HYSYS or Aspen Plus. According to the entire process flowsheet simulation, 35% power reduction and 10% thermal exergy savings can be achieved in the conversion process by MR technology employment under the best-case scenario (ideally water-permeable zeolite-based membrane, isothermal condition and 7500 kPa as the feed pressure).

Product	Formic Acid	Ethanol	Propanol	Methane	Methanol	FT-Product	
Scalability	Very good (CO ₂ E)			Limited (reactor size, piping etc.)			
Energy demand MWh/t _{co2}	4	11	11	10	10	12	
Hazards	Flamable substances			Flamable substances, High Temperatures			
Energy grid integration	Not likely			Natural gas grid	Fuel as MtG	Fuel	
Process complexity	One step process (CO2E)			Several react	Complex downstream		
Market volume	Base chemical			Base chemical and energy carrier			
Suitability as substitute	Direct substitute for base chemicals, with effort as energy carrier			Direct substitute for base chemicals			
				And energy carriers	With effort as energy carrier	And energy carriers	

Table 20: Overview of different decisive factors for the different products and the associated synthesis routes.





Figure 41: Comparison of the different fuel synthesis routes for the various products.

8 CONCLUSION AND OVERALL COMPARISON

To compare the different fuel production possibilities, some metrics are introduced. The first being the energy demand normalized on the required CO2 for the fuel. This number is useful to quickly asses how much energy is needed for a given CO2 capture plant, since in this scenario the size of such a DAC unit would be determined by the size of the ventilation system. A second interesting metric is the Energetic Efficiency I_E. This value is calculated by dividing the chemical energy output by the required energy to produce the specific fuel:

$$\mathbf{j}_{E} = \frac{\mathbf{HHV}_{Fuel} \cdot \mathbf{Produced Amount of Fuel}}{\mathbf{I}_{Fuel} \cdot \mathbf{Produced Amount of Fuel}}$$

Energy demand

With HHV being the Higher Heating Value of the produced chemicals. The energy consumption for the production of those hydrocarbons is based on the syngas produced by the thermochemical cycle (TCC), since this is the most novel process and a promising competitor with direct utilisation of renewable energy.

This comparison shows very similar efficiency values for the products. Interesting is the very low energy demand per t of CO2 for the production of formic acid. Since the overall efficiency is comparable to the rest, this could be a reasonable product for use in a DAC-context. Especially as a base chemical and not as an energy carrier, formic acid seems useful. The high use of CO2 in comparison to the chemical energy obtained contradicts the thought of a low carbon fuel. However, if the objective is to use the activated carbon as a chemical feedstock, formic acid could perform well. Since the other products are rather similar in terms of energy efficiency and demand per t of CO2, other factors should form the basis for a decision.



An overview of possible factors is given in Table 20. A major criterion is the scalability. The size of the DAC should be determined by the HVAC system to get the maximum yield from the available airstream maximizing the synergy. Therefore, the electrochemical conversion seems to be an elegant solution. Similar to the PEM-electrolysis the individual cells are relatively small and the capacity is created by stacking those cells. This also leads to an easy scalability. CO2-e cells have the additional benefit of directly creating the desired product, instead of the need for several intermediate steps, like the syngas production in case of Methane, Methanol or Fischer-Tropsch-Synthesis. The last one has the benefit of producing hydrocarbons that can substitute established crude oil products. Unfortunately, FTS needs a complex downstream process to convert the linear hydrocarbon chains into useful products. This could compromise the installation into urban scenarios. Methanation and methanol synthesis seem to be a better option here with Methane having the additional benefit of direct grid injection in most parts of Germany. It can also be used in block-type thermal power stations, for a form of energy storage. Methane could therefore be an efficient energy carrier from places with a dark dull situation to places with available solar and wind energy. Methanol on the other hand has the potential of being the base chemical for a variety of the process industry while it could still be used as a fuel substitute if converted with the MtG-process.

Methane and Methanol therefore seem to be viable solutions for a decentralized production plant in the near future. Electrochemical direct conversion has additional benefits in terms of simplicity. In the far future, those cells could overtake the production plants, but are still in the development process.



OUTLOOK

This report represents a collection of technologies for a circular carbon economy, based on opinions of the experts of the Helmholtz-Initiative Climate Adaptation and Mitigation. The technologies are shown in a neutral way without stressing the influencing surrounding factors too much. The constrains and benefits are shown, but no definitive decision to one technology is done. From this perspective, several tasks for the future of the circular carbon economy are exposed.

First, it is clear, that the different technologies are all their own TRL. While BECCS is rather developed and does not need major research, technology schemes like decentralized DAC are still in a very early stage. Therefore, more research is needed for a great scale deployment. On a basic level, new and better materials, such as catalysts, could be improved, to further increase the efficiencies of the processes. In addition, detailed studies of the used biomass or optimal operating conditions could contribute to better and more capable of competing in the market. On the technological site of the R&D spectrum, the plants of the DAC scheme need to improve vastly to be competitive. Mainly the associated cost needs to decrease, by using mass fabrication or new manufacturing techniques like additive manufacturing. This could allow for small standardized units, which could be produced in great numbers at competitive costs. Those new fabrication techniques could also increase the efficiency and decrease the complexity of the processes, since no industry standards must be met.

Alongside these R&D efforts, the plants need to be investigated further in their environment and especially in the context of a future energy grid. This would require strengthening the capability of the modules to be operated dynamically. Not only could they then serve as an energy sink if renewable energies available exceed the grid capacity, they could also follow the diurnal cycle of renewable energies. Additionally, the produces hydrocarbons could serve as energy storage, giving back energy in small power station, when demand exceeds the available green power.

Besides the technological development, the awareness and knowledge of those circular carbon technologies in the society need to increase as well. BECCS had some major problems in the past to be accepted on a broad basis within the public. There cannot be a big rollout, if the people do not agree with those changes. On the other hand, the topic of P2X is not present in the public today at a satisfactory level. Here the awareness needs to be raised, so that this scheme is in the heads of the responsible people, when projects in the context of a carbon-neutral energy system are planned

All this information and development is still on a rather abstract level. To reach the practical planning level a scenario-based assessment is required. With defined boundary conditions, a definitive selection of technology options is possible. Such constrains can be the existing power source, the available land at its fertility or the available space. Especially the decentralized DAC approach with integration into ventilations systems lead to a strong dependence on existing infrastructure and building characteristics. From usage patterns of the building to intensity and duration of irradiation, there are a lot of constrains and influencing factors when it comes to an urban small system. From here, the intended use can be defined. The goal could be to capture a maximum of CO2 from the air or to provide a maximum or a stable supply of usable product. Based on such assumptions a detailed scenario can be created with either a BECCS scheme or a DAC based scheme. Combinations are possible as well depending of the scenarios. Those scenarios can then be implemented into a larger model to see, where the most effort should be invested.

Overall, this report serves as a bases and overview for future research and development. Experts of all field in the context of a circular carbon economy should use the results, to implement BECCS and DAC based P2X-schemes into future scenarios and as a base to decide the direction of future efforts and research.





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