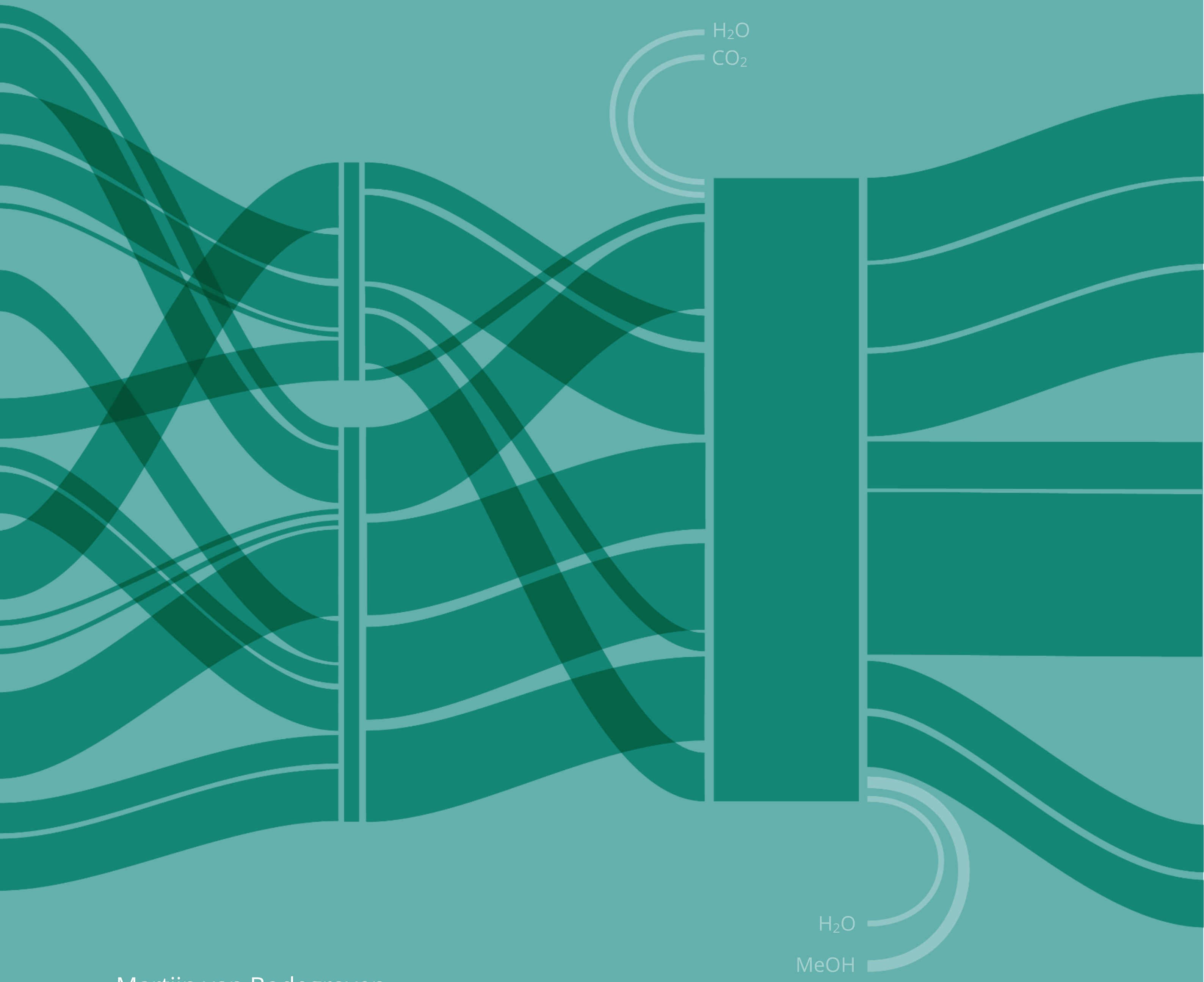
Air to methanol via the micro-plant approach

An ex-ante life cycle assessment



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Master thesis Industrial Ecology
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Preface and acknowledgement

The capture of carbon dioxide, whether it is from point sources or the atmosphere, has been a topic of controversy between the public, climate scientists, technology developers, and policy makers. It seems that beyond the IEA and IPCC, carbon capture still has a ways to go in proving its worth and establishing its place in our ongoing energy and climate transition.

To follow R. Buckminster Fuller's philosophy that change doesn't come by fighting the existing reality but by building new models that make existing models obsolete, a model for our relationship with greenhouse gasses seems long overdue. I imagine a new role for carbon dioxide in our society's energy and material metabolism where it is no longer viewed as a wasteful by-product but instead as a kind of inverse resource where its depletion is rewarded and atmospheric 'replenishing' is discouraged. A hint towards this type of thinking can be found in the European Emission Trading System, though it clearly does not provide a balanced framework. Such new model would have a distinct place for initiatives and technologies that valorise CO_2 capture and utilisation, as it is the current most practical example of treating CO_2 as a resource.

Rushing new technologies without considering environmental extensions is of course never advisable, and a great deal of work is yet to be done. As the tiniest cog in the wheel and mostly as personal learning opportunity early in my career, I hope that this thesis in one way or another is a step in the right direction.

On a personal note, I would like to extend my gratitude to all the people who have helped me before, during, and at the finish of my thesis. Above all, to my friends and family who have offered a listening ear, and have helped me manage expectations and set priorities. Especially to Eva, who has continuously supported me and who is always able to find fun and adventure in every challenge, and to my parents Joop & Heleen who have undertaken the considerable effort of reading the report and have offered their guidance in crucial moments.

The Team at ZEF BV, who hosted and facilitated the thesis project, have also been indispensable both for the project's practicalities and more importantly for the daily positive attitude, feedback and the around-the-clock availability to discuss findings and problems.
Finally, to the members of my graduation committee, who have made my graduation possible through René Kleijn's positive and practical coaching style and Andrea Ramírez Ramírez' unique ability to sieve through data and provide detailed remarks.

Executive summary

Conversion of CO2 to value added products and the microplant approach
The capture of carbon dioxide before or after it is emitted has been regarded as a crucial mitigation pathway to prevent the rapidly increasing accumulation of CO2 in the atmosphere. The valorisation of the captured CO2 into value added products such as methanol provides an additional economic incentive to continue developing these technologies. Zero Emission Fuels B.V. (ZEF) is a company that works on developing a mass-producible miniature methanol plant that houses a Direct Air Capture and CO2-compression unit, an Alkaline Electrolysis Cell, a Methanol Reactor, and a Distillation unit. The expected potential benefit the microplant-concept is its ability to be mass-produced, allowing for economies of scale in production and the rapid upscaling of CO2-based methanol plants. The microplant is furthermore fully autonomous and is designed to be integrated en-masse with a photovoltaic power plant, enabling the production of methanol in remote areas that receive high annual solar irradiation.

Using life cycle assessment to investigate the environmental profile of microplant-based methanol
The production and operation of all sorts of infrastructure and upstream activities to facilitate CCU-based chemical production may introduce a variety of trade-offs. As has been argued and proven in previous works, the production of value-added products from CO_2 can be challenging and their general sustainability cannot be guaranteed. To validate the microplant-concept from an environmental perspective, a research project was therefore executed with the goal to establish the environmental profile of the microplant, to identify hotspots for impact mitigation, and to assess the position of the microplant's environmental profile in relation to results of comparable technologies reported in literature. To realise these objectives, this project applied life cycle assessment using an ex-ante approach, envisioning the microplant in full operational scale (3250-4000 units, in Oman) as opposed to it's current lab/pilot-scale technology level.

The microplant is assessed in a range of potential future states using an ex-ante perspective
Instead of describing a potential future technological state with a deducible probability, the LCA in this study works on the principle of multiple scenarios on the short term (~5 years) and medium term (~10 years) relying on pessimistic/neutral/optimistic expectations about the future technological development of the microplant-concept. The process data and other foreground data was received from the technology developers and is based mostly on estimations, process calculations, and early experimental results. The scenarios are compiled from a number of semi-structured interviews with the developers and topical experts. Provided data could not be extensively verified and was only put into perspective with data from comparable larger scale systems.
To highlight the direct integration of the microplant with photovoltaic panels and to prevent temporal mismatches within the LCA model, the PV system is also subjected to ex-ante modelling. The future background database by Mendoza et al. (2018/2020) is used to consider the general future state of the material and energy production sectors in alignment with the shared socio-economic pathway scenarios in the IMAGE model.

A negative cradle-to-gate Climate Change impact score
The impact assessment of the future PV-powered air-to-methanol plant, suggests that it is likely that methanol produced using this approach will exhibit a low climate change impact along its production chain. Especially compared to conventional methanol produced via the steam reforming of natural gas the microplant approach shows a clear climate change mitigation potential. The analysis in this study furthermore demonstrates that the temporary sequestration of CO_2 in methanol leads to a negative impact score at the factory gate between -0.92 and -1.09 kg CO_2 equivalent per kilogramme of methanol compared to 0.64 kg CO_2 eq. for NG-based methanol. If the inevitable re-emission of captured CO_2 is considered, for example via combustion, the climate change impacts will lie between 0.29 and 0.47 kg CO_2 eq., compared to 2.01 kg CO_2 eq. for conventionally produced methanol.

Methanol produced via the microplant approach leads to a higher demand for metals
The microplant route towards low-carbon methanol production is associated with a strongly increased material demand for metals and to a lesser extend for plastics. For one, supplying the high energy demand for the capture CO_2 and production of H_2 with electricity from photovoltaic panels is responsible for a large part of the material demand. This general tendency of renewable energy technologies to require more metals compared to fossil-energy technologies has been widely studied. In addition, a significant strain on the material demand originates from the required production of thousands of microplants, including their subsystems, to reach

significant production volume. In this study it was analysed that under the short term neutral technology scenario the microplant approach approximately demands between 1-2x more iron, 4-6x more copper, 9-12x more aluminium, and 17-18x more nickel per kilogramme of methanol. Such additional demand was consistently found for other metals such as lead, silver, cobalt, zinc, tin, and platinum, and for a variety of plastics. As the microplant is still in early development, these numbers are faced with large uncertainties, yet provide a valuable first indication of the material demand.

The capture of CO_2 likely puts additional strain on the environmental profile beyond climate change
Using polyamine sorbents for the process of capturing CO_2 from the atmosphere subjects these sorbents to stresses leading to degradation and emission of degradation compounds. Using a scenario-based approach, and relying on rough estimates about the implications of sorbent degradation for emissions of ammonia, this study shows that such emissions are significant in the overall environmental profile and lead to potential damages on ecosystem quality and human health. Low sorbent-lifetimes of under 1-2 years cause significant additional burdens both due to emissions and the demand for additional sorbent manufacturing. The current study is too limited to scope the extend and severity of DAC-related impacts and to recommend appropriate mitigation strategies. It has nonetheless shown that these emissions cannot be overlooked and should be subject of future research.

Environmental trade-offs between impact categories are apparent
Although a distinct benefit in the climate change and ozone depletion category is identified, the aforementioned aspects of the technology lead to potential adverse effects on categories regarding ecosystem quality and human health compared to conventional production. Depending on the analysed technological development scenarios and their key assumptions, the microplant-methanol shows higher impacts in between five and nine of the twelve analysed environmental impact categories. In these categories, most notably the freshwater ecotoxicity, eutrophication, (non-)carcinogenic effects, and respiratory effects categories, the microplant impacts are typically a factor of 2 to 4 higher. Chapter 6&7 discuss the nuances of contributions.

Design changes and further developmental research could soften the environmental trade-offs
To mitigate the disadvantageous differences between the environmental profiles of microplant-methanol and conventional methanol a number of strategies can be adopted in the areas of energy demand, energy supply, material use, and CO_2-sorbent upgrading/emission prevention. Energy optimisation remains a key focus for the developers though literature review indicates that the energy demand of the microplant is higher (around 10-20%) compared to other CO_2-based methanol systems. Previous LCA works highlight the opportunity and value of heat integration and AEC efficiency optimisation to mitigate impacts. On the supply side, opting for low-impact energy mixes in PV production and consulting PV environmental profiles may offer additional prospects. As there is simply a larger material demand for the subsystems and control systems, optimisations beyond the reduction of Nickel are more difficult to envision in this area and the developers are generally recommended to consider the importance of materials and to continuously seek opportunities for material optimisation.
Lastly, optimising the CO_2-sorbent to reduce degradation and prolong its lifetime would both limit emissions and production-related impacts. Alternatively, washing systems commonly applied in point-source capture could be integrated in the microplant to limit the emissions of ammonia.
Overall, the combination of impact mitigation efforts will make it less probable that significant trade-offs in two of the twelve impact categories will occur. In four out of twelve categories however, will neither mitigation efforts nor the general optimistic technology scenario be enough to turn the impact score in favour of the microplant. The relative severity and importance of these trade-offs will need further research.

A first look at the environmental profile and flagged hotspots, though more research is crucial
In this research project, a microplant concept for low-carbon methanol production was analysed that is awaiting the move to full pilot scale. It remains a real possibility that process parameters such as the energy demand are underestimated, that the overall process emits gasses that were not yet estimated/included in this study, or that gases are emitted that currently lack characterisation factors. As the microplant progresses to higher technology readiness levels, both experimental primary data and technology expectations will predict the eventual future performance and emissions with increasing accuracy. Life Cycle Assessment should then be used to continuously evaluate the environmental significance of updates throughout the development trajectory.

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1. Introduction

1.1. *Introduction*

Society and hydrocarbons
Society's energy metabolism has long been primarily made up of energy embedded in hydrocarbon sources, starting from the foraging of widely available biomass in early societies up to the mining of fossil hydrocarbon deposits that were formed in the combined effort of ancient biological process and slow geological processes. With the introduction of Bakelite in 1907 as the first fully synthetic thermoset, hydrocarbons also started to secure their place in the global material metabolism. From the early twentieth century onwards these compounds have been used in the chemical industry to produce a large portion of the intermediate products that have been instrumental for global welfare growth. Indeed, the importance of hydrocarbon compounds for the resource and energy base of modern day society can hardly be overstated.

In the present day the supply for the energy and material metabolism of our world (i.e. chemical industries and energy sectors) is still dominated by primary products of fossil origin. The massive cumulative use of fossil products results in the accumulation of greenhouse gasses and various pollutants in the atmosphere, biosphere and hydrosphere. Via multiple pathways these emissions lead to a variety of adverse impacts on the quality of ecosystems and human health. The combined effect endangers the welfare of current and future generations (IPCC, 2018).

The obvious and drastic need for a more sustainable energy and material metabolism has led to a slow but noticeable global movement of decoupling greenhouse gas emissions from energy production (IEA, 2020). The same movement is more difficult to envision for the chemical industry as both the needed process energy and process feedstocks are best supplied by hydrocarbon products (Kätelhön et al., 2019). This leads to the current expectation that the chemical sector will be the driving force for the global oil consumption by 2030 (IEA, 2019a). Other large sectors that will continue to rely on fossil sources of hydrocarbons are the heavy industry for iron and cement production and the long distance transport sector (IEA, 2020). It is therefore unlikely that the demand for hydrocarbon products will come to cease, in fact it is more likely to showcase continued growth while heading towards the second half of this century (IEA, 2020).

CCU as potential sustainable pathway
One approach to a more sustainable future is the capture and use of CO_2 as feedstock for the production of chemicals and fuels. This class of technologies is called Carbon Capture and Utilisation, or CCU, and encompasses those technologies that aim to obtain a benefit from extracting and using CO2 to produce products for various sectors with hard to abate emissions (Baena-Moreno et al., 2018). Potential additional benefits of CCU lie in the sourcing of carbon dioxide beyond industrial point sources, for example from biogenic sources or from ambient air (Direct Air Capture / CCS). Both these options have the potential to contribute to the active removal of CO2 from the atmosphere through temporary sequestration in chemical products, thereby preventing atmospheric CO_2 accumulation from similar fossil-based alternatives. Current projections from the IEA consider CCUS technologies as fundamental supporting strategy to realise mitigation pathways (IEA, 2020). The ambitious Sustainable Development Scenario for example relies on the use of about 1 Gt of CO2 to produce fuels and feedstocks by 2070 (IEA, 2019b).

The methanol economy and renewable methanol
Using excess carbon dioxide as feedstock in recycling processes to produce fuels, synthetic hydrocarbons and other chemical products shows potential to decouple welfare growth from fossil product consumption (Olah, Prakash & Goeppert, 2009). One promising pathway, as discussed in 'The Methanol economy' by Nobel-price winner George A. Olah and colleagues, relies on the initial synthesis of methanol and derived dimethyl ether (DME) from CO_2 to provide a number of key benefits. Both these products can be used as transportation or industrial fuels, thus providing a route towards low-carbon practices for carbon-intensive sectors. Methanol and DME can furthermore be converted into ethylene, propylene, and other a variety of other chemicals for further intermediary products, consumer products, and pharmaceuticals (Olah et al., 2009). In addition, methanol can be used as liquid energy carrier for energy from renewable sources which bypasses the cooling and pressurizing needs of hydrogen while potentially offering more flexibility in energy conversion (Alberico &

Nielsen, 2015). George A. Olah and colleagues capture the merits of methanol in the following quote; "*Practically all hydrocarbon fuels and products currently obtained from fossil fuels can be efficiently obtained from methanol, which in turn, as emphasized, can be produced by the chemical recycling of natural or industrial CO_2 sources.*"

Conventionally, almost the entire global methanol supply is produced via syngas synthesis which relies heavily on the use of natural gas or coal (Goeppert et al., 2014). An increasing share is produced by converting biomass to methanol, though concerns about land use, biodiversity loss and competition with food crops are increasingly being voiced (IRENA, 2021). Alternatively, methanol can be produced using CO_2 and H_2 as feedstocks via numerous thermochemical, electrochemical, and photochemical routes, each varying in degree of technological maturity.

Multiple renewable methanol projects are currently in place or under development, the majority being based on the principle of biomass conversion. Some initiatives aimed at creating methanol using renewable electricity (renewable e-methanol) are receiving more attention as well. The most noteworthy are the Icelandic Carbon Recycling Institute which started in 2011 (CRI, 2020) and the Chinese Dalian institute for Chemical Physics methanol plant which runs exclusively on electricity from a 10MW solar PV plant (Ye, Tian, & Liu, 2020). These projects have as disadvantage that they generally require large investments, are difficult to scale, and have to deal with challenges of intermittently available renewable energy.

1.2. *The Zero Emission Fuels project & research goal*

A small-sized methanol plant as tech start-up

Since a few years, the university town Delft in the Netherlands is home to a technology start-up called Zero Emission Fuels B.V. (ZEF) that has the goal to produce carbon neutral and affordable methanol. The start-up is currently pursuing a distinctive route towards the synthesis of methanol by developing a small-sized methanol plant (from hereon called the 'ZEF MeOH concept') that requires only sunlight and ambient air, and that is designed to be mass-produced (ZEF, n.d.). Powered by PV panels the micro-plants can be arranged to form a micro-plant farm containing many thousands of units. Theoretically the modular approach allows easier scale-up to fit the demand, therefore offering more flexibility compared to larger industrial methanol plants. Because the ZEF concept needs just air and sunlight the future microplant farms can be built in convenient low cost locations where solar irradiance is plentiful. In addition, the micro-plant farm concept enables dynamic operation, meaning that methanol is only produced when electricity from the PV panels is available. This approach allows the technology developers to lower the initial capital investments and solve the issue of scalability, which is often encountered by projects that engage in the chemical recycling of carbon dioxide into methanol (G. Olah et al., 2009).

At the moment the concept is still in development, with multiple engineering teams working on each of the individual units. According to the founders the micro-plant concept is currently at a stage where many initial uncertainties are resolved and the design is nearing the phase where it can be implemented in a test plant (J. van Kranendonk, personal communication, 28 December, 2020).

A need for further research

As illustrated by its name, the Zero Emission Fuels project is aimed at producing carbon neutral renewable methanol. To substantiate the developments towards this goal the project stakeholders have identified the need for an up to date assessment of the environmental impacts of the proposed system. In part, such assessment would also heed the call in recent literature for more research into the environmental impacts of CO2 conversion technologies, adding to the growing body of research in this area (e.g. Artz et al., 2018).

An earlier study has already been performed for the ZEF concept which gave a valuable first insight into the potential of the ZEF microplant in terms of the reduced environmental impact compared to conventional fuels. However, the reason for updating and expanding the assessment consists of three parts; first, the ZEF concept has undergone numerous design iterations which renders the initial assessment out of date. Second, the large uncertainties that are typically associated with assessments of low-TRL technologies were not comprehensively assessed and communicated. Third, the results were not compared to a competitive reference system of alternative means of renewable methanol production which would have facilitated a discussion on the place of the ZEF concept in the global future methanol market. Therefore there is a need for a new assessment performed with a focus on the abovementioned topics.

During the preparation for this study, no published literature has been found that review the potential of a modular and mass-producible approach to the capture of CO2 and conversion into methanol. It is therefore the core goal of this study to explore the potential environmental merits and pitfalls of this approach, while taking into account the wishes for information from the stakeholders of this project.

1.3. *Goal & Research approach*

It is widely recognized that early environmental assessment of emerging products or technologies provide a foundation for research and development decisions to steer the development trajectory of the product towards more environmentally favourable outcomes (Arvidsson et al., 2018). The solar-to-methanol farm concept based on the micro-plant design by ZEF B.V. currently exists at a low manufacturing readiness level and the final design at market introduction can still be informed by the outcomes of an environmental assessment. The main objective of this study is to provide these insights in the environmental impacts of the ZEF Concept. The secondary objective is to provide material for a discussion on the competitiveness of the micro-plant approach compared to other pathways of low-carbon methanol production. The outcomes of the proposed research will assist the technology developers in communicating their efforts towards important external stakeholders. This coincides with the '*micro-level decision support*' decision-context as explained in the ILCD handbook and cited by Ramírez Ramírez et al. (2020) which stands in contrast with the 'meso/macro-level decision support' for LCA projects that study the large scale changes in systems due to the introduction of a new system. The intended goal thus limits itself to the study of the direct environmental impacts of the ZEF concept and not the changes it instils in the socio-technological landscape.
The objectives above can be captured in the following research question;

"What is the environmental impact reduction potential of methanol produced at a full scale solar-to-methanol micro-plant farm compared to conventional methanol production?"

In order to gather enough material for a discussion on the research question, a number of sub-questions are formulated. First, it is necessary to establish the environmental impacts of the concept as it stands today. No fully functional prototype has yet been developed though the components work individually, an overview of the complete theoretical design is provided by the technology developers. This initial version is modelled and assessed as the first step in the research approach.
Secondly, it is important to analyse the contribution of relevant design parameters and the role of potential design alternations. Although the making of design and development decisions heavily depends on their financial implications, the resulting information also allows the inclusion of environmental impacts as an important criterion;

1) What technological parameters have the highest impact on the environmental performance and what are promising areas for optimisation?

As the current ZEF concept is situated at a low manufacturing readiness level, it is useful to analyse what the future may bring in relation to the environmental performance of the design. Future dynamics that could influence the environmental profile are for example trends in the background energy mix and/or raw material extraction and processing, and general performance improvements of the ZEF concept that come with increasing technological experience and maturity. The assessment should assess the potential future state of the technology instead of its limited current state. In other words, a prospective approach is needed that can be captured in the following question:

2) How will the environmental profile of the Z.E.F. concept change when it is developed further towards market introduction?

At market introduction the ZEF concept will have to compete with other means of methanol production in the technological landscape. An initial analysis of how the ZEF microplant might be positioned in relation to its competitors in terms of environmental performance can therefore a valuable tool to potentially guide technological development. The need for such analysis is reflected in the last sub-question;

3) How do the results of this LCA-study compare to the results found in literature on comparable methanol production technologies?

The exact content and research approach of all of the above sub-questions will be elaborated in detail in the methodology chapter.

1.4. *Outline of this study*

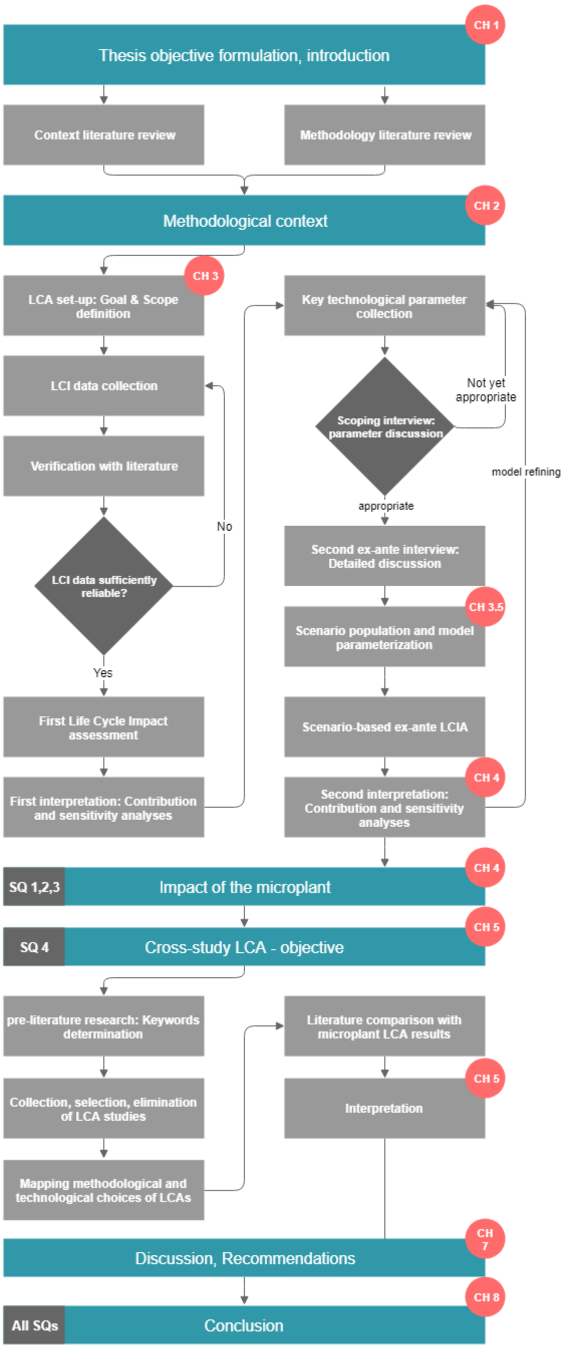


Figure 1: Research flow diagram followed in this study.

LCA for environmental assessment

The general research approach of this study is visualised in figure 1. The method of choice to answer the previously introduced sub-questions is Life Cycle Assessment (LCA). Due to its wide use in studies with comparable objectives, LCA has been developed to a nearly institutional state and is widely recognized as the best tool to holistically evaluate the environmental performance of product systems. The foundation for, and implication of, the use of LCA will be elaborated in following chapters.

LCA and emerging technologies

Despite its relative maturity the LCA methodology is faced with some challenges regarding the specific analysis of emerging technologies and carbon capture and utilization systems (van der Giesen et al., 2020; Ramírez Ramírez et al., 2020). Therefore, an initial action performed within this research project has been the analysis of available literature surrounding these challenges, this is visualised in the figure under 'CH 2' which stands for chapter 2.

Iterative research approach

LCA is in part characterized by an iterative approach of goal & scope definition, data collection, populating of the life cycle inventory, impact assessment, and interpretation to assess if the model needs refining. The iterative process is visualised in the figure in two stages, the initial stage stands for the first version of the model that forms the foundation for all the other work. The second stage uses insights from the first model to streamline the data collection process for the approximation of the microplant in hypothetical future states. The outcomes of this second analysis attempt to answer the first three sub-questions.

Literature result comparison and validation

To answer the question about how the microplant might perform in comparison to comparable technologies reported in literature, a cross-study LCA analysis is performed. This analysis, which is basically an extensive literature analysis, collects data from published LCA studies combined with their methodological assumptions and considerations. The results are then used to understand the microplant in relation to its competitors. The combined effort of these major steps allows for the answering of the main research question and the drafting of recommendations and conclusions for the technology developers at Z.E.F. B.V.

02 | Context & Background

2. Context and methodology

As previously introduced the main objective of this research project is the assessment of the environmental profile of methanol produced by the microplant concept as designed by Z.E.F. B.V. The goal of this chapter is both to provide the study with the contextual background required for a foundational understanding of the main objective, as well as setting apart the method used to achieve the objective. Section 2.1 will first discuss the relevant global background, section 2.2 then provides a brief overview of the methodological context, after which 2.3 and 2.4 elaborate on the exact methodology that forms the backbone of this study.

2.1. *Contextual background*

2.1.1. Definition of low-carbon methanol

Low carbon vs renewable methanol can lead to confusion

The methanol production pathways with a high impact mitigation potential with regards to conventional methanol production are subject to a multitude of umbrella terms. The most frequently named terms are 'low-carbon-' , and 'renewable-' methanol. The latter for example, is used in the influential recent joint report on Renewable methanol by the IRENA and the methanol institute (IRENA, 2021). In the report the term 'renewable methanol' is used to denote all sorts of methanol production pathways, including those production schemes that utilise point-source CO_2 (i.e. CO_2 from industrial combustion and chemical processes). The same report reserves the term 'low-carbon' methanol for hybrid processes that rely both on fossil sources and that utilise emission mitigation processes such as CO_2 injection or H_2 boosting with renewably produced H_2.

Fact is that the term 'renewable' implies the use of resources that are replenished on a human timescale. Using the term 'renewable' for methanol that still predominantly relies on CO_2 from the combustion of fossil resources is therefore unjustified. This work therefore prefers the use of the term 'low-carbon' methanol.

The definition of low-carbon methanol in this study is sub-divided

The definition of low-carbon methanol followed in this study is as follows; The methanol production pathways that attempt to substitute the currently dominant fossil feedstocks (natural gas, coal) with 1) feedstocks of largely non-fossil origin and/or 2) feedstocks that show mitigation potential by utilizing by-products from other product systems, while 3) making use of low-carbon energy sources for the delivery of process energy. Part one of this definition entails feedstocks obtained from the hydrosphere, atmosphere or to a lesser extend the biosphere. The second part aims to describe the use of by-products that otherwise would cause more immediate downstream adverse impacts. Low-carbon methanol is furthermore characterized by the potential to improve the environmental performance with the gradual decoupling of national energy systems from fossil resource use.

Low-carbon methanol is the umbrella term that spans across multiple categories that are characterized based on the choice of feedstock, the route of feedstock processing / methanol synthesis, and the choice of energy provision. The exact terminology for these categories differs in literature (e.g. Olah et al. 2006; IRENA, 2021; Artz et al., 2018; Delikonstantis et al., 2021). In this research, a distinction is made on the basis of core-feedstocks;

- CO_2-based f-methanol: Methanol derived from captured CO_2 from various sources, and hydrogen delivered in various forms of fossil origin.
- CO_2-based e-methanol: Methanol derived from captured CO_2 from various sources, and hydrogen retrieved from water electrolysis.
- Bio-based methanol: Methanol derived from feedstocks that are *exclusively* of biotic origin.
- Waste-based methanol: Methanol derived from feedstocks of mixed abiotic and biotic origin, mostly considered as waste-products from other product systems.

This terminology is used throughout the report, though CO_2-based methanol is discussed in more detail than biomethanol. For a more elaborate discussion on biomethanol, the reader is referred to appendix H.

2.1.2. Conversion of CO_2 to methanol

The ZEF methanol microplant, which stands at the core of this study, falls under the CO_2-based r-methanol typology. This section provides a brief overview of the various technologies and production pathways that reside in the CO_2-based methanol class.

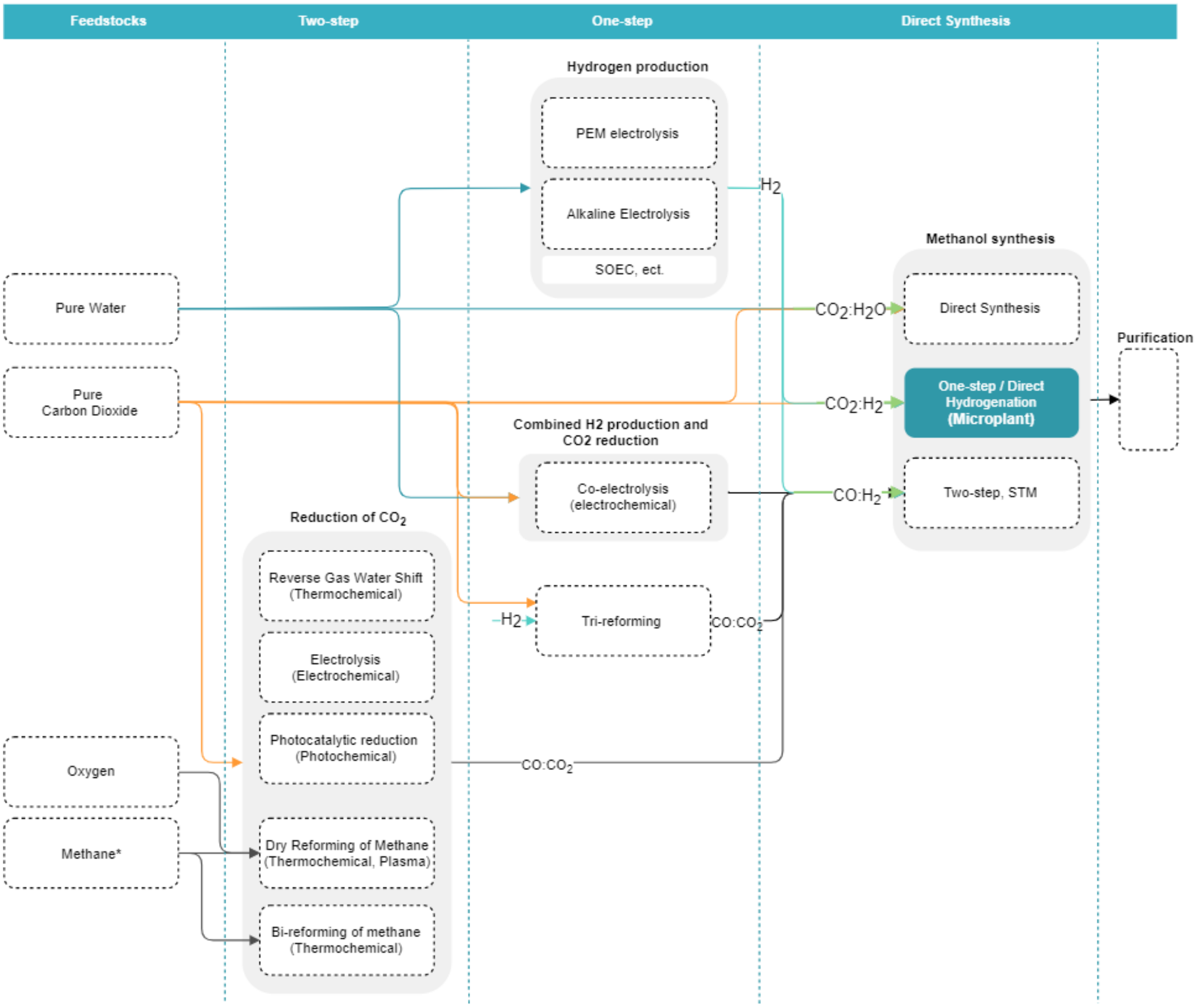


Figure 2: Overview of the technological pathways to low-carbon methanol production from basic feedstocks. The microplant is a case of thermocatalytic direct hydrogenation of CO_2 marked by blue in the figure.

The methanol synthesis step (MS): a variety of key production pathways

The conversion of CO_2 into value-added products can be realized via a multitude of technological pathways varying in the number of key process steps, energy sources, catalysts, and general process design and optimization. In this section, the various pathways are aggregated to a few archetypical means of methanol production. Due to the high technological maturity of methanol synthesis processes, the type and composition of available feedstocks often determine the design of the production chain. Yet to understand the variety of production chain designs, it is best to start at the methanol synthesis step and traverse upwards in the supply chain via multiple routes. Considering water and carbon dioxide as main feedstocks, methanol synthesis can occur via a two-step process, a one-step process, and a direct synthesis process (figure 2).

MS - Syngas conversion as the currently dominant methanol route

The two-step synthesis, also called the 'Syngas-to-methanol' (STM) process, is the current most prevailing methanol synthesis pathway and is characterized by the catalytic conversion of syngas at pressures between 50-100 bar and temperatures of between 200-350 degrees Celsius (Marlin, Sarron & Sigurbjörnsson, 2018). The process consists of two key processing steps, focusing first on the reduction of the chemically inert CO_2 to form synthesis gas with hydrogen, and the subsequent synthesis of methanol from the syngas. Most industrial applications of the two-step approach utilize a $Cu/ZnO/Al_2O_3$-based catalyst as main promotor of the reaction and selectivity towards methanol. High selectivity (i.e. > 99%) can be achieved by catalyst optimization, conversion at higher pressures, and tweaking of the syngas composition (Ye et al., 2019).

MS - Direct hydrogenation of CO_2 into methanol as promising pathway

The one-step synthesis process, also called 'Direct hydrogenation (of CO_2)', is the direct application of un-converted CO_2 in the methanol synthesis reactor. Due to its independency from fossil resources, the one-step process is relatively new and less technologically developed compared to its conventional counterpart. Though the conditions of the reaction do not differ much from the two-step approach, direct hydrogenation is typically associated with lower single-pass conversion. In addition, the higher presence of water has negative effects on the lifespan of the catalysts. Therefore one of the key challenges is developing new and improved catalysts to increase the methanol selectivity of the reaction, and new reactor designs (Stangeland, Li & Yu, 2020). Despite of its disadvantages, the one-step approach exhibits multiple significant benefits such as a higher overall thermodynamic efficiency (Artz et al., 2018), fewer unwanted by-products that require energy-intensive separation steps (Marlin, et al, 2018), and the promise of simpler production chains. These benefits lead to the testing of the one-step process in numerous pilot- and industrial-scale projects. The most famous example being the Carbon Recycling International plant in Iceland (CRI, n.d.).

MS - Combined carbon dioxide and water conversion as low-TRL alternative

Direct methanol synthesis circumvents the need for separate hydrogen electrolysis and in theory allows methanol synthesis from carbon dioxide and water using a single process design. Direct synthesis using electrochemical processes is mentioned in some articles (e.g. Adnan & Kibria, 2020) but on closer examination the academic foundation for direct synthesis seems to be lacking. Masel et al. (2021) describe the electrolysis of carbon dioxide with water to form c1 and c2 chemicals, which so far has seen decent developments in lab-setting. Nabil et al. (2021) use a direct synthesis alternative in their LCA on the electrochemical conversion of CO_2 into hydrocarbon products, albeit based on low TRL lab-scale results.

Other mentions of direct synthesis are related to the development of photocatalytic processes using complex cell designs of highly specialised semiconducting materials that can directly reduce CO_2 into methanol. These cases of 'artificial photosynthesis' stand for a line of research that to this date has only lead to lab-scale production of methanol (e.g. Yamin Wu, n.d.; Jia et al., 2017) and suffer from poor charge recombination, poor stability, and poor selectivity (Guil-López et al, 2019). Generally, examples of direct methanol synthesis only exist at very low TRL's due to the variety technological challenges that are difficult to abate (Wu et al., 2019). For this reason the direct synthesis of methanol from CO_2 and water is not further considered in this study, though it may show interesting developments over the next decade.

Reduction of CO_2 (C-R) for syngas production: incumbent and new routes

Under the two-step approach, a syngas ratio of 2:1 between hydrogen and carbon monoxide is considered ideal for efficient synthesis under conventional process design (Artz et al., 2018). If carbon dioxide forms the main feedstock of the total industrial process, it therefore first needs to be converted to carbon monoxide. One of the most well-studied processes of CO_2 utilisation for the downstream synthesis of methanol is Dry Methane Reforming, taking CO_2 instead of steam for the reforming of methane into syngas. DRM is a highly endothermic reaction between CO_2 and CH4 that requires high temperatures of around 750 degrees Celsius (Artz et al., 2018). Most examples of DRM-based methanol are thermocatalytic, relying on thermal energy to support the reaction (Pan et al., 2020). In addition to fossil-based thermal energy, solar-thermal or electro-thermal processes are possible and have been studied in recent literature as a means to reduce the environmental impact of DRM-based methanol (e.g. Delikonstantis et al., 2021). Alternatively, low-TRL applications of direct photocatalytic DRM have been studied but so far have not resulted in effective syngas production (Tahir et al., 2019).

Besides the challenge of sourcing thermal energy without significant environmental burdens, DRM is also subject to challenges such as the catalyst deactivation as result of the deposition of carbon and feedstock impurities (Artz et al., 2018). Regardless, the DRM offers the possibility to turn methane from various renewable sources (e.g. biomass) into widely usable hydrocarbon products while also offering a pathway for CO_2 utilisation.

C-R: Reverse gas water shift reaction

A second process that is well-introduced in the chemical industry is the reverse Water Gas Shift reaction (rWGS), an equilibrium reaction between carbon monoxide + water and carbon dioxide and hydrogen. In the chemical industry the WGS reaction is used to produce a variety of chemicals (i.e. ammonia, hydrogen) and to tweak or compliment ratios for syngas production. The (reverse) formation of carbon monoxide and water in the rWGS reaction is an endothermic process, requiring temperatures of between 200-250 °C or 310-450 °C depending on the type of catalyst. The advantage of the rWGS process in the methanol production chain is its relative flexibility to produce carbon monoxide for higher methanol yields, though it comes at the cost of having to produce hydrogen which in itself is an energy intensive process. The CAMERE process, a relatively high TRL CO_2-based e-methanol project from the Korean Institute of Science and Technologies, uses the rWGS reaction as key component of it's two-step methanol production process (Joo et al., 1998).

C-R: Bi-reforming

A relatively new method of arriving at syngas is the combined double steam methane reforming and subsequent dry methane reforming in a process called 'bi-reforming of Methane' or BRM. Alternatively, tri-reforming of methane (TRM) is also possible, adding a Partial Oxidation of Methane process (POM). Potential advantages of this route lie in the immediate use of heat from the exothermic POM process for the endothermic BRM and TRM. It furthermore shows potential for waste-gas utilisation from specific sources such as manure gasification. Contrary to the earlier mentioned processes, BRM and TRM have not been studied extensively as method of GHG remediation method (Cunha et al., 2020). The same is the case of LCA studies, only few cases exist where BRM and TRM are considered in parallel to other processes (e.g. Nguyen & Zondervan, 2019).

C-R: Electrochemical reduction

As alternative to the currently incumbent CO_2 reduction technologies the electrochemical conversion of CO_2 to CO has received considerable attention due to its potential to only use renewably produced electricity. In a CO_2 electrolysis unit, a CO_2 stream with a predetermined humidity level is led to the cathode and water is circulated with an electrolyte into the anode. At the cathode CO_2 reacts with water to form CO and OH-, after which the OH- passes through the membrane to the anode where it forms water and oxygen. The result is a continuous flow of carbon monoxide and oxygen if current is applied to the unit. Current densities within industrially available electrolysers are typically between 200 and 500 mA cm^{-2} and show Faradaic efficiencies of more than 95% (Masel et al., 2021). The current densities, Faradaic efficiencies, and the cell voltage form the most important operating parameters for electrolysis. Again, the choice of catalysts and reactor design proves to be the main challenge in this technological niche and most recent research efforts are therefore focused at improving the tweaking of electrolysis units to produce specific products. Lifetimes of CO_2 electrolysers under continuous load are still relatively short, between 2 and 7 years depending on the current density in the unit (Masel et al., 2021). Such considerations are especially relevant when comparing it to conventional means of CO_2 reduction. Electrochemical conversion via electrolysis has recently reached a decent level of technological maturity with the introduction of commercially available low-temperature electrolysis units and major developments in the long term stability of catalysts (Masel et al., 2021).

C-R: Photochemical reduction

One step lower on the TRL ladder lies the photochemical reduction of CO_2. Though often combined with the parallel splitting of water in combined reduction and oxidation (see next section) the photocatalytic CO_2 reduction can also be seen as separate technology. It consists of 1) the adsorption of light to generate electron and hole pairs in a semiconducting material, 2) the separation of the photogenerated electrons and holes, 3) The adsorption of CO_2 on the surface of the photocatalyst, 4) the surface electrochemical reduction reaction to form CO, and 5) product desorption (Wu et al., 2017). Depending on the design of the process and the choice for the photocatalyst, other products can be produced as well. Regardless of significant advances in the technological development of photocatalytic CO_2 reduction, the technology still suffers from low reaction activity and product selectivity (Wu et al., 2017). Only lab-scale applications of the photocatalytic conversion of CO_2 into more useful products are currently available.

Single process co-production of CO and H_2
As briefly introduced in the previous section, electro- and photochemical conversion routes offer the possibility to combine the reduction of carbon dioxide with the splitting of water. Co-electrolysis is the electrochemical route for the combined production of CO and H_2. At the cathode the CO_2 combines with hydrogen to produce CO and water, or reacts with water to form CO and OH-. At the anode, water splits into H_2 and oxygen. As the electrochemical reduction of CO_2 is in many ways similar to water electrolysis, the co-electrolyser design shows great similarities with water electrolysers. Efficiencies differ per electrolyser type and were found to be generally greater for Solid Oxide Cells (SOCs) with 96% conversion efficiencies at 20 bar, compared to Proton Exchange Membrane cells (PEM) at 78% and Alkaline Electrolysis Cells (AEC) at 74% (Araya et al. 2020). Amongst others, the typical challenges for co-electrolysis are the hindering of reactions by contaminants, the decomposition of electrodes (Artz et al., 2018), the low single pass conversion requiring multiple loops, and the formation of unwanted by-products (Araya et al. 2020). Still, the potential efficiency gains of co-electrolysis lead to the gradual development of increasingly more efficient processes. Siemens (Siemens, n.d.) has recently shown that it is well underway of commercializing co-electrolysis units.

Similarly, photochemical reduction of CO_2 and water can be combined in a single cell. The introduction of co-catalysts causes the electrons and holes in the photocatalysts to both drive half-reactions for CO_2 reduction and water splitting. The combination of these processes could even lead to more optimal cell designs (Wu et al., 2017). However, relatively poor performance under normal light conditions could require solar concentrators, leading to additional equipment requirements (Artz et al., 2018). Combined photochemical production of CO and H_2 is currently at a lower TRL than co-electrolysis.

2.1.3. The ZEF Microplant concept

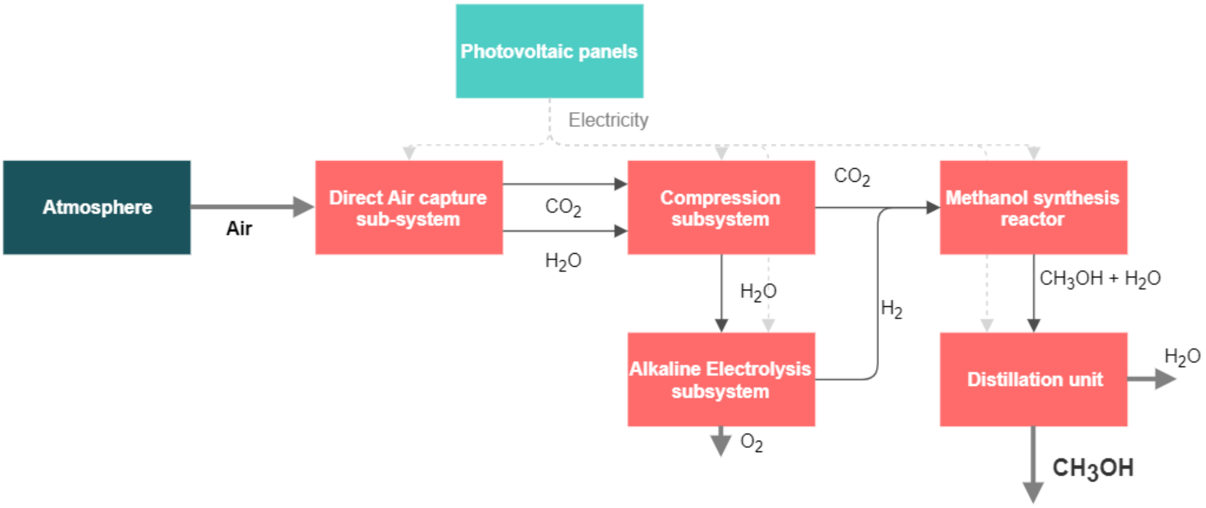


Figure 3: ZEF microplant, schematic overview

The concept designed by ZEF is a modular, mass-producible miniature methanol plant that houses five distinct systems to successfully capture CO_2 and H_2O from the air and convert it into methanol. Large scale methanol production can be realised by constructing arrays of microplants connected by pipelines to collect the produced methanol. Such 'farms' are preferably located in areas with high annual solar irradiation, thereby making use of methanol as convenient energy storage medium and generally increasing the efficiency of the photovoltaic system. In this section the microplant is briefly elaborated, the LCI of this LCA study discusses the individual mass and energy flows in more detail.

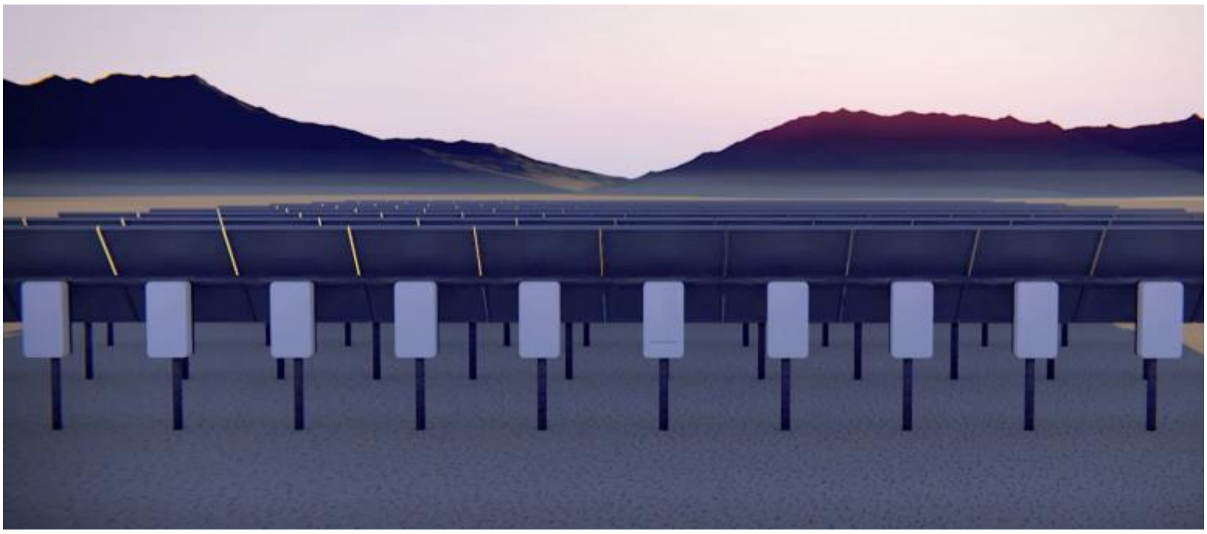


Image 1: Artistic impression of the microplants integrated with the PV farm. Credits: Zero Emission Fuels B.V. 2021

The DAC system: Continuous capture of carbon dioxide using a polyamine-sorbent
During sunlight hours the DAC unit receives electricity from the solar panels to capture air, extract the CO_2 (and H_2O) molecules, and send the CO_2 to the FM system for compression. Currently operating DAC units are often batch operated, meaning that every few hours the unit stops collecting air and needs time to dissolve the CO_2 that has been captured in a medium for transport. The DAC unit in the microplant system opts for a continuous capture system, meaning that as long as the DAC unit receives electricity from the panels during sunlight hours, it continuously collects air and simultaneously captures the CO_2 and sends it to the FM system for compression. Continuous operation has some key benefits for the microplant. For one, the mechanism is simpler and potentially more energy efficient.

In the DAC system the CO_2 and H_2O are absorbed from the airflow into a sorbent which is then pumped into a desorption chamber where the sorbent is heated to release the captured CO_2 and water. To improve the speed of absorption into the sorbent a diluent is introduced in the attempt to lower the viscosity of the sorbent as it becomes thicker due to its loading with CO_2.

The AEC system: Alkaline electrolysis
Zero Emission Fuels B.V. have opted for an Alkaline Electrolysis Cell (AEC) for the production of hydrogen. Simplified, an AEC cell is characterized by two electrodes placed in a liquid alkaline electrolyte (in this case Potassium Hydroxide, KOH). A diaphragm in between the electrodes separates the oxygen formed on the anode and the hydrogen formed on the cathode while hydroxide ions can flow freely through the diaphragm. ZEF currently develops a self-pressurized electrolysis system with natural electrolyte recirculation. This entails pressurization by the built-up of continuous gas production in the cell. The hydrogen resulting from the electrolysis therefore does not have to be pressurized before it is fed into the methanol reactor. The electrolyte is circulated automatically and does not require an additional pump. Like all systems, the AEC unit starts running when electricity is available and is responsible for supplying the methanol reactor with enough hydrogen to support the formation of methanol.

The architecture of the AEC can be divided in the individual cells, the stack, and the system. The cells work as previously described, the stack houses the amount of cells required to deliver the hydrogen demand under set electrochemical parameters. The system includes auxiliary equipment for the cooling of the stack, the actuator for energy delivery to the stack, and the control systems.

The Fluid machinery (FM) system: Compression of carbon dioxide
The methanol reactor operates at a pressure of 50 bar, requiring the carbon dioxide captured in the DAC unit to be compressed to this optimum pressure level. This is the task of the fluid machinery subsystem which consists of a three-phased array of pumps and valves designed to both dry the CO_2 flow from the DAC unit and compress it to 50 bar. In the first phase of the FM system, two parallel drying chambers contain silica to extract water from the CO_2 flow. Solenoid valves provide the option to steer the gas flow both in both directions. This enables the alternation of drying/water desorption modes in the drying chambers, hence the parallel design to allow for continuous drying and water desorption. The wet gas return from the FM system is sent back to the DAC unit where most of the water ends up in the column to the AEC.

The Methanol Synthesis reactor (MSR): direct hydrogenation of CO_2 with hydrogen
In the methanol synthesis reactor the captured and compressed carbon dioxide is hydrogenated with hydrogen over a catalyst at 50 bar and under elevated temperatures. The transport of gasses within the MSR is driven by natural convection, internal pumps are therefore not necessary. A major additional benefit of this type of methanol reactor is that theoretically it can run in an autothermal mode, which entails that the heat released in the exothermic reaction of hydrogen and carbon dioxide into methanol meets the heating needs at the inlet of the reactor for raising the temperature of the hydrogen and carbon dioxide mixture to the required levels. This type of methanol reactor is based on the work by Bos & Brilman (2015) who first described the type of methanol reactor and its potential to efficiently convert CO_2 to methanol for the storage of renewable electricity. High yields (>99%) have already been reported by ZEF in lab-setting.
To prevent the accumulation of nitrogen in the reactor and to occasionally measure its contents, the reactor has a purge flow that vents approximately 2% of the feedstock gasses to the atmosphere.

The Distillation unit (DS)
In the MSR, water is co-produced with methanol in a 1:1 ratio. In the DS system the mixture is separated in a distillation column to produce 99.8% pure methanol and 99.9% pure water.

Integrated in a photovoltaic plant without the need for grid connection
The energy needs of all subsystems are satisfied by photovoltaic panels. Under the current design the microplant will be attached directly under a group of photovoltaic panels that on average produce sufficient electricity to continuously produce methanol under daylight hours. The type of solar panels that will likely be used in the first microplant farm are based on bi-facial m-Si PERC solar cells (Chint Solar, personal communication, n.d.). Bifacial solar panels have an advantage over mono-facial panels because electricity is generated if both or either of the panels' faces is illuminated. Mono-crystalline panels are furthermore typically associated with higher efficiencies. Bifacial m-Si Perc panels are currently mass-produced and some plants have already been constructed using this particular type of panel. *The direct integration of the microplant with the photovoltaic system eliminates the need for an external inverter and reduces the need for extra external wiring and electrical infrastructure. The methanol farm furthermore does not require grid connection and can run solely on photovoltaic electricity.*

Image 2: Artistic impression of the ZEF solar-to-methanol farm. Credits: Zero Emission Fuels B.V. 2021

03 | Methodology |

3. Methodology

The life cycle assessment of emerging technologies, and more specifically CCU technologies, is not without its challenges. In this chapter the existing literature is reviewed on the analysis of these challenges and the efforts set forward to meeting the challenges in practical LCA work. The first two sections of the chapter form a summary of key works in this field, the sections after the summary are more practically oriented and detail how challenges were addressed in this research project.

3.1. *Ex-ante Life Cycle Assessment*

LCAs are valuable in the development of emerging technologies but guidelines are lacking
To this date most LCA studies are performed on an ex post basis, meaning that the analysed system is already in place and the needed data can be extracted by observing its processes (Cucurachi et al., 2020). Yet, it is well known amongst technology developers and LCA practitioners alike that the power to influence and improve the environmental impact of a product system is greater earlier in its development process rather than later (Arvidsson et al., 2017). The mismatch between the typical application of LCA and the application of the tool for those cases that could benefit most from it, has led to a large variety of case studies where Life Cycle Assessment was performed in an ex-ante fashion as opposed to ex-post (e.g. as analysed by Arvidsson et al., 2018; Cucurachi et al., 2018). Most ex-ante LCA's typically study 'emerging' technologies that are in an early phase of development but extrapolate and model this technology in a theoretical future and more developed phase.
Modelling an emerging technology in an 'emerged' phase inevitably requires a consideration about how the performance aspects of the technology can and will change. Similarly, in a comparative assessment with an incumbent technology the analyst should also take into account the development of the analysed alternative. In that sense the studies cannot be said to predict the future but instead to explore scenarios in which the technology may operate in order to guide R&D decisions (Cucurachi et al., 2018; van der Giesen et al., 2020).
It furthermore appears that the research and modelling approach in ex-ante LCA is not consistent across case studies and that there is a lack of clear guidelines as to what methods are appropriate for such studies (Moni et al., 2019; Bergerson et al., 2020). The next section reviews some key articles with the goal to identify the main challenges that need to be tackled in this research project.

Challenges of ex-ante LCA: Defining a consistent future context as foundation of an ex-ante study
Naturally the temporal aspect of the scope definition plays a significantly larger role in ex-ante LCA as compared to conventional LCA. The extent to which the LCA practitioner wishes to extrapolate the development of an emerging technology impacts all other choices that directly influence the LCA results. Multiple temporal effects can be identified. For one, the analysed emerging technology will have a unique development trajectory that is influenced by internal and external drivers and barriers. In turn, the possibility exists that the emerging technology influences its direct and indirect market which furthermore complicates the prediction of its development (Cooper & Gytowksi, 2018; van der Giesen et al. 2020). Bergerson et al. (2020) note how LCA analysts often do not include a distinction between technology and market maturity and instead mostly focus on emerging technology in mature markets, therefore omitting the effects of new markets. The authors of both papers therefore argue that it is crucial to explicitly define the technology's level of technological and market maturity in order to secure a proper scope definition. The definition of a clear future context is arguably one of the main challenges of ex-ante LCA (van der Giesen et al., 2020).

Choosing a functional unit consistent with potential future services of a product or system
The true basis of assessment and comparison in LCA lies in the careful consideration of what functions a product, service or system actually provides, as opposed to a focus on a particular quantity of the product or service. The impact assessment then provides an idea about which option provides the service most effectively from an environmental perspective. The prediction of the service that an emerging technology may provide can be challenging. In some cases the technology developers may not be certain which market they will tend to (Cucurachi et al., 2018), whereas in other cases the emerging technology may be introduced into multiple markets thus providing multiple services (Ramírez Ramírez et al., 2019; e.g. van der Giesen et al., 2014). For both situations the definition of the functional unit remains a deliberate choice that includes an implicit assumption about the future of the technology. Such choice then impacts the choice of an incumbent technology for a

comparative assessment, making it challenging to execute a proper comparative assessment (Hetherington et al., 2014). The establishment of a functional unit that is in line with the services that the emerging technology provides, and that is appropriate for the research objectives is a clear challenge of ex-ante LCA and requires thorough consideration (Cucurachi et al., 2018; Moni et al., 2019; van der Giesen et al., 2020).

Data unavailability and data scale-up are the core challenges of ex-ante LCA
Conventional LCA makes thankful use of existing LCI databases that have been compiled through real-life historic analysis of the respective processes. It takes time to build and verify these databases which is why these databases are not always up to date (Cucurachi et al., 2018). Conventional ex-post LCA also has the advantage of being able to observe real life process data for the foreground system, thereby providing the LCA analyst with enough sources of data.
Naturally, the analysis of a technology in a future context does not allow a LCA analyst to make use of conventional sources of data. This added problem of data availability in ex-ante LCA is widely recognized (Hetherington et al., 2014; Arvidsson et al. 2017; Cucurachi et al. 2018, Moni et al., 2019; Bergerson et al. 2020; van der Giesen et al., 2020). The available data for the modelling of the foreground system is often based on specific experiments and cases on lab-scale and can therefore not be used to model the foreground system in an operational context (Cucurachi et al. 2018; van der Giesen et al., 2020). Whereas missing data is otherwise supplemented by data from repositories this is more difficult for ex-ante LCA because such databases are non-existent or incomplete for the materials used in the emerging technology (Moni et al., 2019). Other secondary inventory data from scientific articles, patents, or from expert interviews suffers from the same problem; there either is a lack of appropriate data or data only describes the technology aspects under specific conditions (van der Giesen et al. 2020). In cases where technology developers can provide an estimation of operational data, data is likely to be in the form of probability distributions instead of point values which furthermore complicates the use of data for the Life Cycle Inventory (LCI) (Cooper & Gutowski, 2018).
Besides missing, incomplete, or non-representative data future-oriented LCAs have to deal with the challenge of scale-up. In practice, important process improvements occur when a technology moves to a more mature phase which has an enormous effect on its environmental performance and LCA practitioners have to take these effects into account (Moni et al., 2019). The process of manipulating available data to fit a future scenario is often found to lead to the further aggravation of the model uncertainties (Hetherington et al., 2014; Arvidsson et al. 2017; Cucurachi et al. 2018, Moni et al., 2019; Bergerson et al. 2020; van der Giesen et al., 2020). Although LCA analysts can rely on available theories and methods to project the data in a future timeframe it seems impossible to do so without relying on subjective assumptions (Cucurachi et al., 2018; van der Giesen et al., 2020).

Conventional impact methods might not cover future impacts
Typical for ex-ante LCA is that that certain characterization factors for new materials are not included in the available characterization models which could lead to the omittance of certain materials that, by nature, are important for the assessment of novel technologies (Cucurachi et al., 2018, Moni et al. 2019, van der Giesen et al., 2020). The lack of coverage of new materials by existing impact categories could therefore mask a part of the environmental profile of an emerging technology, making it look more favourable in a comparative assessment with an incumbent technology.

Ex-ante LCA is faced with ‘unknown unknowns’ going beyond conventional uncertainty analysis
The compounded uncertainty of assumptions and data/scenario modelling leads to numerous uncertainties in the interpretation of the LCA results. According to Hetherington et al. (2014) and Cucurachi et al. (2018) a proper communication of the variability and uncertainty of the results are crucial for the usefulness of LCA for technology development. Uncertainty analysis in conventional LCAs allows open communication about the uncertainties that are associated with the assessment. Because the life cycle inventory and characterization factors are known, the confidence of the results can be calculated to a certain degree. However, ex-ante LCA adds a new layer to the uncertainty of LCA results because of knowledge gaps due to lacking data or simply because predictions of the future are inherently uncertain (van der Giesen et al. 2020). Uncertainty analyses in ex-ante LCAs are therefore prone to providing an incomplete picture of the certainty of the results by only addressing the ‘certain uncertainties’ and not the ‘unknown unknowns’. The differences in ‘types of uncertainties’ are captured by the typology of van der Giesen et al. (2020). Based on the typology by Wynne (1992) the authors make a distinction between; “*a) risk, (system parameters and probabilities are known), b) uncertainty (system parameters are known, but not the probability distributions), c) ignorance (neither system*

parameters or probabilities are known, and d) (the future development is inherently undetermined)". The analysis of emerging technologies, especially those with low technology readiness levels, should be paired with an additional discussion focused on identifying overseen impacts and disadvantages of the technology (Moni et al., 2019).

The challenges of ex-ante LCA require this study to look beyond conventional LCA methodologies
It should be clear by now that ex-ante LCA lacks the widely accepted methodological framework of conventional LCAs. This new way of using LCAs in the R&D of emerging technologies causes numerous methodological challenges that require the LCA analysist to look for new ways of filling in data gaps, calculating impacts, and communicating the inherent uncertainties of the LCA results. This literature review is extended in the appendixes where some solutions have been set forth that were be used to shape the methodological approach of this research project. The practical implication of these solutions are listed in section 3.3.

3.2. *Life Cycle Assessment of carbon capture and Utilisation technologies*

Although CCU pilot projects are rapidly introduced, most CCU technologies with promising outlooks currently exist at low Technology Readiness Levels. The Life Cycle Assessment of these technologies therefore are subject to many of the same challenges as described in the literature review of ex-ante LCA, especially regarding data collection and the management of uncertainties. Additionally the use of carbon dioxide as feedstock introduces more methodological challenges. As will be introduced, such challenges are more relevant for cases where CO_2 is captured from point sources and lesser so for cases of direct air capture such as in this study. Nonetheless, for the sake of completeness this overview also discusses point source capture and its implications.

Environmental benefits of CCU products are not guaranteed
The argument for the thorough environmental assessment of emerging CCU technologies is threefold. First, the capture of CO2 from various sources is a relatively new technological field and both the energy and material requirements (e.g. for the recycling of the sorbent and infrastructure) can be high (Meunier et al. 2020; Rosental et al. 2020). Secondly, the activation step of the chemically inert CO2 molecule for further downstream use requires high energy input and/or energy demanding co-reactants (Artz et al. 2018; Zimmermann et al. 2020; Ramírez Ramírez et al. 2020). Depending on the energy source the high energy demand might lead to unexpectedly high impacts, the same is the case for the production of the co-reactants and the use of catalysts. Lastly, although the global warming potential of new and emerging technological systems is considered one of the most important impact categories, other impact categories may highlight important trade-offs. Examples are a higher impact results in toxicity impact categories due to the use of sorbents that produce toxic by-products (Garcia-Garcia et al., 2021). In addition, cases can be imagined where the CCU system under analysis performs worse than potential alternative systems that provide the same services (van der Giesen et al. 2014). It is therefore crucial that a proper reference system is constructed to understand the environmental benefits or pitfalls of the system (Ramírez Ramírez et al. 2020). The arguments above show that the sustainability of CCU systems is not guaranteed and is in need of proper assessment.

System boundaries of CCU LCAs are critical to the impact assessment
A first challenge for the life cycle assessment of CCU systems, as discussed by von der Assen, Jung and Bardow (2013), is the proper assessment of CO_2 as feedstock and its contribution to the global warming impact score. In some early examples of LCAs on CCU technologies CO_2 feedstock was only regarded as a negative emission, disregarding relevant upstream emissions of the CO_2 capture process (Von der Assen et al. 2013). This links to the challenge of system boundaries as discussed by Ramírez Ramírez et al (2020) and Zimmermann et al. (2020) in their guidelines for Life Cycle Assessment of Carbon Capture and Utilisation technologies. Both guidelines express the need for a full life-cycle approach, from the energy and material requirements for raw material extraction up until the final in- and outputs of end-of-life processing. A cradle-to-grave assessment provides a thorough outlook on the impacts of CCU technologies, including the burdens imposed by the carbon capture process. However, when a CCU product provides exactly the same functions as an incumbent technology, the inclusion of downstream process only adds to the complexity of the LCA model, while not providing additional insights. Upon analysis of a large collection of LCA studies on CCU technologies, Garcia-Garcia et al. (2021)

found that indeed the majority of analysed studies adopt a cradle-to-gate boundary and state that only those processes should be excluded that are identical for the compared alternatives. Ramírez Ramírez et al (2020) and Zimmermann et al. (2020) provide space in their guidelines for a cradle-to-gate approach, though under the condition that this choice is explicitly explained and discussed with regards to the function that the CCU system or product is expected to provide.

An additional challenge to the study of CCU systems lies in the impact assessment of the temporary nature of carbon storage, for example in a chemical product. Although it may be useful to store CO_2 for a period of time from a climate change perspective, conventional LCA has no way of dealing with such temporary storage and only calculates the emissions over the products' entire lifecycle (Von der Assen et al., 2014; Artz et al., 2018; Garcia-Garcia et al., 2021). There is an ongoing discussion about time-corrected global warming potentials to account for this effect. If these are not available, the duration and amount of carbon stored should be reported in the LCA study as it can influence the interpretation of the results (Von der Assen et al., 2014; Artz et al., 2018; Garcia-Garcia et al., 2021).

CCU projects might offer non-conventional services

Like discussed in the review of ex-ante LCA literature, the definition of the function that the technological system provides forms the foundation for the research. Van der Giesen, Kleijn and Kramer (2014) analysed the impacts of producing synthetic hydrocarbon fuels from CO_2. The authors noticed that the assessment was complicated by the fact that the hydrocarbon products did not facilitate a singular function but up to four simultaneous functions. Similar remarks are made by Zimmermann et al. (2020) and Ramírez Ramírez et al. (2020), stating that as the technology matures, alternative functions/use-scenarios can arise that change how the captured carbon could be re-released and how other substances are emitted. Some recent examples of LCA studies apply multiple functional units in order to assign a performance metric to the multiple services that a CCU system provides (e.g. Liu et al., 2020) though still often only one use scenario is taken into account. Zimmermann et al. (2020) and Ramírez Ramírez et al. (2020), advice to determine the functional unit for CCU systems based on the CCU goal (i.e. chemical, fuel, or energy storage) and its comparison with an alternative system, product or technology.

The accounting of carbon dioxide over product systems largely determines impacts

One of the key challenges specific to CCU technologies lies in the impact allocation of CO2 for the case of point source capture (Von der Assen et al. 2013; Ramírez Ramírez et al., 2020). The CCU technology considers the CO2 as a feedstock whereas the primary emitter of the CO2 considers it as a waste product. The question that remains is how to allocate the CO2 emissions amongst these systems. According to the ISO guidelines for LCA system expansion is the preferred way to deal with this question (i.e. the multi-functionality hierarchy) which is generally emphasized in literature on LCA of CCU (Garcia-Garcia et al., 2021). However, there are cases where system expansion is either not desirable or possible regarding the projects' circumstances/ resources (Ramírez Ramírez et al., 2020).

Contrary to Von der Assen et al. (2013) who call the issue of allocation highly subjective, Ramírez Ramírez et al., (2020) argue that the solution to allocation differs per case. For an addition of a CCU plant to an existing emitting industrial plant all impacts should preferably be allocated to the primary emitter and the reduction in CO2 emissions should be allocated to the CCU plant, i.e. a 100:0 allocation approach. All emissions at the point of the CCU plant should then be allocated to the CCU plant. For the case of a differently operating emitting plant as the result of a CCU plant installation, the same rules apply but the impact changes due to the CCU plant installation should be allocated to the CCU plant. The last case, in which a CO2 emitting plant is built together with a CCU plant, Ramírez Ramírez et al (2020) advise to use the same allocation procedure while using Best Available Technology (BAT) to model the CO2 emitting plant. In each case, a sensitivity analysis is recommended by the authors to account for potential short and long term changes in the analysed system (Ramírez Ramírez et al., 2020).

The (100:0) allocation approach is reflected in case studies, such as the study by Rosenthal et al. (2020) and Fernande-Dacosta et al. (2019) where the authors exclude the CO2 point source from the system boundaries while allocating all impacts due to carbon capture to the CCU plant. The important distinction is that, when assessing the system with a cradle-to-grave boundary, the captured carbon is eventually re-released at the end of the life cycle. The end-of-life emissions should be part of the system boundary of the CCU plant (Ramírez Ramírez et al., 2020; Zimmermann et al. 2020).

This review of the challenges of CCU LCAs is used in the cross-analysis chapter of this study. In addition, it helps set the context for the LCA that has been performed.

3.3. *The approach to ex-ante challenges*

3.3.1. Ex-ante LCA

Does this study require an ex-ante LCA approach?
First of all, let's establish that the research goal at hand matches in fact with the goal and scope of an ex-ante LCA. For this purpose, the definition by Cucurachi et al. (2018) is used that defines ex-ante LCA studies as those that 1) scale-up an emerging technology using estimations of the future performance at full operation scale, and 2) compare the emerged technology at scale with the evolved incumbent technology. The outline of this study attempts to do both, as the microplant currently merely exists at lab-scale and the LCI will therefore rely on global assumptions of its performance at market introduction. Secondly, the methanol produced by the microplant will be compared to the incumbent (i.e. conventional) means of methanol production to gauge where trade-offs may occur. The research task in this work therefore can be classified as an ex-ante LCA.
This is not to say that this study will attempt to achieve a breakthrough in the field of ex-ante LCAs, the primary goal is the evaluation of the microplant and the wider potential of sustainably produced methanol.

Scenarios preferred over probability distributions to capture future technological states
Regardless, this methodological section will rely on previously published literature on ex-ante LCA regarding meeting some of the challenges that are typical for this prospective research goal. On an abstract level, two schools of thought seem to exist within the ex-ante LCA community. On one hand, some researchers attempt to accurately predict the future of a technology by using a wide variety of tools with the added goal of providing a sense of probability to the envisioned future state of the technology. The other approach accepts the inherent uncertainty of the future and instead attempts to capture this variability in a range of future states of the technology using consistent assumptions. The latter might include a discussion on the probability of the future states but will steer away from providing any quantitative indication. Overall it seems like this second approach, characterized by the construction of scenarios, is preferred in most cross-study papers on ex-ante LCA (e.g. Cucurachi et al., 2018; Cucurachi et al., 2020; van der Giesen et al., 2020; Bergersson et al., 2019).

Cornerstone vs. what-if scenarios; technology or systems perspective
The practice of scenario modelling for ex-ante LCA is subject to as many interpretations as the term ex-ante itself but key common elements are identifiable such as the definition of alterative future circumstances, the trajectory from the present to the future and the inclusion of future uncertainty (Buyle et al., 2019). In their practical recommendations for ex-ante LCA Buyle et al. furthermore cite the definition of Pesonen et al. (2000) who divide scenario modelling into two main strategies; what-if scenarios and cornerstone scenarios. What-if scenarios are applicable to projects where the engineering of a technology is at the core focus. Key parameters then tend to focus on potential changes in efficiencies or small tweaks in material inputs. The cornerstone approach goes beyond the what-if approach and considers parameters relevant to the system around the technology, thereby also focussing on the socio-economic context that includes dynamic drivers such as technology adoption. The case as provided by Zero Emission Fuels B.V. is a special one in the sense that the socio-economic context might not be as relevant in comparison to more radical emerging technologies that have the potential to disrupt, for example, the general societal energy management as is the case for novel means of hydrogen production. The project studied in this work concerns a case where a company produces a new product that is mostly based on an aggregation of already proven technologies. The product will furthermore be mass-produced, indicating that technological improvements occur on a batch basis and not on a case-by-case incremental basis that would for example be seen in the development of larger electrolysis plants. It is therefore assumed that the what-if/engineering approach to scenario construction is largely suitable for the goal of this study, meaning that scenario modelling will consist of collecting parameters related to the practical side of the technology's performance.
Often coupled to what-if scenario modelling is the consideration of extreme situations, where future situations of the technology are envisioned based on consistent assumptions about the potential worst performance of the technology, as well as its best (Cucurachi et al., 2018). The remaining range between these future states

provides a ‘window of performance’ that is more likely to contain the eventual real performance of the technology in a given time frame. This best/worst case approach is also recommended by Müller et al. (2020) in their guidelines of for LCAs on CCU technologies as a means to capture some of the uncertainty coupled to new technologies. The use of such scenarios in this study is elaborated in the goal & scope definition.

Population of scenarios through structured expert consultation
The question that remains is how to populate these scenarios. Van der Giesen et al. (2020) establish that guidance for the modelling of specific new technologies is extensive but that more general guidance for other technologies is absent. The authors recommend that LCA practitioners organize structured discussions with technology developers and topical experts on the future expectations of new technologies. They furthermore warn that it should not be expected that perfect and correct answers will be provided but that instead enough information can be collected to investigate hypothetical scenarios of technological development. Indeed, in discussions with senior LCA experts it was confirmed that in practice the workshops/interview leads to practical results for LCA modelling (A. Ramírez Ramírez, personal communication, n.d.). On the contrary, more in-depth and detailed discussions about very specific technological aspects was found to result in vague and unstructured discussions with unusable outcomes. This is in part due to the vast topical knowledge of experts, allowing them to lose track of the general objective in detailed discussions. However, the depth of knowledge of experts allows the discussion of more abstract expectations that still are based on an intuitive understanding of the topic at hand. The engagement with experts will thus form the backbone of the ex-ante phase of this research project.

3.3.2. Data collection for foreground ex-ante modelling

Sensitivity analysis to streamline expert consultation
Data collection for the representation of current and future states of the technological performance of the microplant has been done in the form of semi-structured interviews with the technology developers at ZEF and topical experts for specific parameters. Semi-structured interviews are an often used method in LCAs. It is characterized by having just a few predetermined questions or a checklist with topics that need to be discussed, leaving room for flexibility and organic discussion. In this research project, interviews were held in group sessions and in private conversations with the technology developers. Group sessions allowed a critical debate on certain topics and resulting conflict leads to occasional tweaking of initially voiced opinions. On the other hand private conversations tend to avoid a group effect and leave room for more original contemplation. Guidelines and topics for these interviews were created on the basis of a sensitivity analysis of an early version of the model. The sensitivity analysis identified key contributing factors that required more attention and that could benefit from the knowledge of the experts. Global interview outlines were drafted and generally consisted of two main steps; the initial global discussion of potential future states of the microplant (i.e. a warm-up) and the more detailed discussion on expectations of key technological parameters.

Expert consultations outcomes were verified with basic calculations and literature research
The combined result of group and private conversations led to some variety in opinions between interviewees. Insights and parameters derived from interviews were therefore evaluated in an iterative fashion following the hierarchy of LCI data generation from Parvatker and Eckelman (2019). This hierarchy has been developed with chemical industry cases in mind but can for a large extend be applied beyond these cases. If available, data from the lab scale testing of microplant sub-components was used to evaluate potential improvements. Basic process calculations were then used to validate whether the provided values were realistic and actually resulted in the balancing of in- and outputs to the system. Such calculations were also used / consulted for, for example, the production of the sorbent in the DAC system. Proxies were only used if the specific relevance of that

parameter to the environmental results was expected to be relatively low.

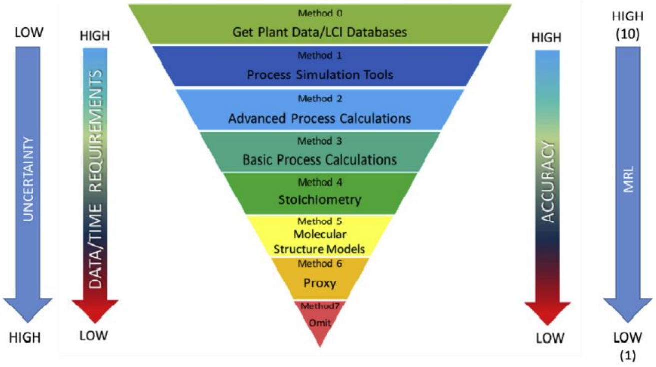


Figure 4 Hierarchy of methods in LCA data generation (from Parvatker and Eckelman, 2019; as cited by van der Giesen et al., 2020)

The data collection for the ex-ante LCA of the photovoltaic system supplying electricity to the microplant was realised using not expert interviews but available roadmaps that provided detailed expectations about parameters unique to photovoltaic systems. The use of industry roadmaps is also applied in cornerstone ex-ante LCA works such as the study performed by Hertwich et al. (2015) and is generally considered to be a reliable source of future data. Expert interviews with the main PV supplier (CHINT solar) of ZEF BV were still held but only as a validation of the values found in the industry roadmaps. The data collection for the PV system will be elaborated in the LCI chapter.

3.3.3. Data collection for background ex-ante modelling

Temporal mismatches between the fore- and background system can lead to incorrect interpretation
The importance of a consistent future-oriented approach to the background system is underlined both in literature on ex-ante LCA (Cucuarchi et al., 2018, Bergersson et al. 2019, Buyle et al., 2019, van der Giesen et al., 2020) and guidelines of the LCA of CCU technologies (Ramírez Ramírez et al., 2019; Müller et al., 2020). For CCU technologies, the dependence on the carbon intensity of many of the background processes (i.e. energy generation, material production) can be very influential and expected changes in national energy mixes might therefore be closely related to the environmental performance of these technologies (Müller et al., 2020). In ex-ante LCA, temporal mismatches can occur between the fore- and background system, leading to over or underestimations of the total impacts.

In this study: IAM-based future background system by Mendoza et al. (2018)
It is therefore important to this research project to include a focus on the background system as integral part. Some LCAs account for changes in the background by updating important background processes with expectations about their efficiency and emissions (e.g. Rosental et al., 2020). The benefit of this partial approach to background system modelling is that the modelling of the databases is limited to just a few key processes. Its obvious disadvantage is that many of the interconnected background processes will not be updated and therefore still partially showcase the temporal mismatch between the fore- and background. As a remedy to this mismatch, research efforts have been directed at creating larger structures containing future parameters on top of currently existing databases such as ecoinvent. The benefit of this holistic approach is that the use of such future databases extends beyond specific case studies. Due to the massive task of updating all relevant background processes in existing database the creation of these future databases is still lacking. Mendoza et al. (2018) however, wrote about their successful creation of background scenarios using the IMAGE integrated assessment model (IAMs) and building on the Shared Socio-economic Pathways (SSPs). This initial study by Mendoza et al. was limited to electricity background changes and it was generally recognized that the LCA community as a whole would benefit from more research into future databases.

The superstructure approach as add-on for the ecoinvent database
For this study, the most up to database from the work by Mendoza et al. was kindly provided by researchers at the centre for environmental sciences Leiden (CML) in the superstructure format (Steubing & de Koning, 2021).

The original data used in this databases was provided by the Netherlands Environmental Assessment agency (PBL) and is fundamentally based on the IMAGE model (Stehfest et al., 2014). The IMAGE computer model is maintained by the PBL and simulates the (environmental) consequences of human activities by aggregating land, energy, climate, and policy models in one framework. The IMAGE model was coupled to the ecoinvent database by Mendoza et al. and aggregated into a single suitable LCI database and scenario package. To the knowledge of the author, this future database is the only one of its kind and the best suitable to ensure consistency between the fore and background systems.

The background model is from hereon called the 3.7.1 superstructure ,regarding its reliance on the most recent ecoinvent 3.7.1. database and the use of the superstructure approach to make the database manageable (Steubing et al., 2021). The 3.7.1. superstructure database is subdivided into multiple scenarios, which are based on the Shared Socio-economic Pathways. The scenarios in the SSPs are based on different future socio-economic projections/political environments and the resulting CO_2 concentrations by 2100. SSP1-1.9 for example stands for the lowest CO_2 concentration end-result by 2100 with an average concentration of 393 PPM. SSP5-8.5 results in a CO_2 concentration of 1135 ppm by 2100. For this research, SSP2.6 is chosen by default. The SSP2.6 'socio-economic family' is not the most ambitious of all families and considers all relevant contextual developments to arrive at a global temperature increase of around 2-2.5 at the end of this century. Other scenarios are used as a sensitivity analysis.

The shared socio-economic pathway 2.6 scenario as main background scenario for the LCA
It is guaranteed that at least the electricity systems in the background model closely mimic the SSP2.6 scenario. Unfortunately transparent documentation of the 3.7.1. superstructure is still lacking. It remains unclear how many of the fundamental sectors (i.e. raw material production) are also affected by the overarching scenarios. However, the database format can be consulted and the amount of processes that have received future parameters seems to far exceed the processes related to electricity in the ecoinvent database. It can therefore be assumed that the database stretches beyond just the electricity sector.

3.4. *LCA Goal & scope definition*

3.4.1. Goal definition

Primary goal: performing the LCA and communicate insights
The intended goal of the LCA performed in this project has been partially discussed in the introduction, yet for the sake of completeness and adherence to the ISO guidelines, it is restated in this section. The main objective of this LCA is to establish the environmental performance of methanol produced by the microplant design concept as designed by Zero Emission Fuels B.V. The microplant is to be assessed in a complete methanol farm configuration of approximately 3250 to 4000 microplants that are supplied with electricity from bifacial mono-crystalline silicon panels directly attached above each individual microplant. The methanol farm is situated in Oman due to its high average solar irradiation, making the best use of the energy carrying potential of the produced methanol.
The analysis and resulting insights will be used for 1) *the communication of the microplant concept by its developers to important stakeholders,* 2) *the identification of environmental hotspots that can be mitigated by design interventions,* 3) *an understanding of the sensitivity of the environmental profile to key technological parameters.*

Secondary goal: Comparing LCA results with literature results
The secondary objective is to provide material for a discussion on the environmental competitiveness of the micro-plant approach compared to other pathways of low-carbon methanol production. This comparative objective is meant to 1) potentially set technological performance targets to increase the competitiveness of the microplant in relation to its direct competitors, 2) identify potential technological considerations relevant to the environmental profile from other low-carbon methanol projects that can be applied to the microplant, and 3) provide stakeholders with an overview of low-carbon methanol technologies.

Life cycle assessment as main method
Due to its tested methodological approach and the vast amounts of prior research work performed by the LCA community it is reasonable to assume that Life Cycle Assessment is the suitable tool to address these research objectives. The available LCA software allows for the collection and quantification of all substance and energy exchanges between the microplant product system and the environment into key impact categories that together compile the environmental profile of the microplant. This process of aggregation into impact categories is crucial in achieving the aforementioned objectives.

The importance of modelling electricity
The influence the energy source on the environmental performance of CO_2-based chemical products is large (Artz et al., 2018; Thonemann, 2020; Garcia-Garcia et al., 2021). Despite the importance of the energy source only a single energy source is modelled in this LCA. The main argument for doing so is that a good representation of the electricity generating system is crucial for the complete assessment of this method of methanol production. Yet, many LCA studies exists, and are continuously published, on novel and promising methods of renewable electricity generation. These studies will do a far better job at predicting future electricity generation than is possible within the boundaries of this study. Still, as a part of this study the results will be viewed such that newly published LCA literature can be consulted and used to get a global indication of what usage of these electricity sources will entail for the performance of the microplant. It is expected that most value can be generated with a focus on the microplant, its operation and its environmental profile.

3.4.2. Scope

Attributional approach to a case study
In order to properly define the scope a first distinction needs to be made between types of future oriented Life cycle assessments. Cucurachi et al. (2018) identified multiple approaches in a review of literature containing elements of future oriented LCAs. Some authors limit their study to the future technological systems and the environmental implications of their future life cycles. Such an approach is similar to what is called an 'attributional' approach in conventional LCA. Other future oriented LCA studies model the effects instilled on the future technology landscape (i.e. consequences) by the emerging technology therefore broadening the scope beyond the future life cycle processes. Such assessments are called 'consequential' and are typically used for

policy support (Cucurachi et al., 2018). The main stakeholders of this project are the technology developers, the primary focus is therefore the direct environmental impacts of the ZEF Concept and not the wider range of impacts it can cause in the technology landscape. It is therefore chosen to adopt an attributional approach to the future oriented LCA and limit the scope to the analysis to the future impacts as the result of the life cycle processes of the ZEF solar-to-methanol farm.

Forward-looking LCAs come with a great deal of challenges that add to the complexity of the project. As stated, the primary aim is to support the technology developers in their R&D and the communication of the micro-plant concept to stakeholders and not to significantly contribute to the state of the academic field of ex-ante LCA. As such, the present state of the art of the academic field will be advised but no radically new methods to mitigate the challenges of ex-ante LCA will be introduced.

Geographical scope: Methanol production in Oman, part production in China

According to Ramírez Ramírez et al. (2020), Müller et al. (2020) and Garcia-Garcia et al. (2021) the geographical scope plays a crucial role in the assessment of carbon capture and utilisation technologies due to the large role of the background system in the total impacts. Although the micro-plant design by ZEF does not rely on grid electricity, the location is still important to upstream impacts. Additionally, the solar irradiance is highly location-specific and will contribute significantly to the total performance of the system. For the solar-to-methanol farm the initial location is set to Oman for its high solar irradiation and its relevance to key stakeholders of this project. The PV panels and most *parts* of the microplant will be mass-produced in China, the life cycle inventory will be modelled accordingly. The geographical scope of the production of raw material is left entirely to the ecoinvent 3.7.1. database used in this study with the exception of the production of the sorbent, which is assumed to be located in Germany. End-of-life processing of the microplant is assumed to occur partially in Oman and in India due to its relative proximity and the presence of efficient waste-processing facilities.

Temporal scope chosen with global technology milestones

Arvidsson et al. (2018) and van der Giesen et al. (2020) motivate the need for a proper decision in the goal and scope definition regarding the temporal aspects of the assessment of emerging technologies. The current temporal scope is set at 2025 and 2030, in line with assumptions about expected milestones technological milestones, the first market introduction of the microplants is expected to be realised around 2025, and technological maturity is expected around 2030. All background and foreground modelling choices are made regarding this temporal coverage. From hereon, the 2025 and 2030 milestones are indicated in the report by 'short term' and 'medium term'. The motivation behind using more global temporal indications is that setting specific dates might communicate a false sense of certainty about the technology by those dates. Instead, many of the assumptions underlying the life cycle inventory are merely the result of expert opinions on where the technology might be on the short and medium term.

3.4.3. Scenarios and envisioned technological states

Following the guidelines by Müller et al. (2020) the scenarios are elaborated here in the goal & scope definition as opposed to later in the impact assessment. The scenarios in this study include variations of the total energy and material demand of the subsystems of the microplant as well as variations in energy and material demand for the production and performance of the photovoltaic system. These variations (i.e. the development in relation to baseline data) are estimated on the short term and on the medium term in line with the temporal scope. Each of these time horizons contains a set of parameters that aims to describe the technology under a pessimistic, neutral, and optimistic development trajectory up until that time. This results in a set of six scenarios, the most important considerations are elaborated:

1. Short term pessimistic (ST-P)
   This scenario describes the technology with practically no technological improvements from its current lab/pilot-scale performance. The overall energy efficiency of all systems is low, the alkaline electrolysis cell for example, has a energy efficiency of 61% in this scenario. The DAC unit also demands about 15% more energy than what the technology developers think is well-achievable. The material demand in this scenario is higher, caused by a larger AEC stack to produce sufficient power and lower lifetime of around 30.000 hours (~10 years). In addition, consumables are also assumed to have a shorter lifetime, including the sorbent (1.500 hours, ~6 months) for the DAC and the catalyst for the methanol

reactor (13.000 hours, ~6 years). Lastly it is assumed that the sorbent degrades rapidly and that a significant portion of the degradation products lead to ammonia emissions.

2. Short term neutral scenario (ST-N)
   The short term neutral scenario envisions the technology according to the key performance indicators that the technology developers have identified for the individual subsystems. In other words, if all goes according to plan, this scenario aims to describe the microplant's performance around market introduction. Some parameters are slightly optimistic, such as a 70% efficiency of the AEC unit and a sorbent lifetime of around 12.000 hours (~4 years). The material demand is lower than the pessimistic scenario due to a smaller stack size and increased stack lifetime (60.000 hours, ~20 years), increased catalyst lifetime (22.000 hours, ~20 years) and sorbent lifetime.

3. Short term optimistic (ST-O)
   The short term optimistic scenario builds largely on the neutral scenario with an added positive assumption about the DAC energy efficiency, assuming that it performs 15% better than the neutral scenario. As has been shown during this research project, this performance increase is very likely. The methanol synthesis reactor is furthermore assumed to run in autothermal mode, meaning that it requires far less energy to maintain appropriate synthesis conditions. The only remaining difference with the neutral scenario is a smaller AEC stack size due to better performing electrodes, and a longer sorbent lifetime of 5 years.

4. Medium term pessimistic (MT-P)
   The medium term pessimistic scenario assumes that the pessimistic short term developments continue on the medium term. The exception is that due to the current research pressure for better electrodes for hydrogen production, it is expected that by the medium term higher performance electrodes will be available and price competitive. This leads to a lower material demand of the AEC unit, an efficiency of 68%, and a stack lifetime of around 87.500 hours (~30 years). The DAC unit is expected to perform relatively bad with the same energy efficiency as the ST-N scenario, and a low sorbent lifetime of around 6.000 hours (~2 years).

5. Medium term neutral (MT-N)
   This scenario encompasses technological development as the developers assume to be realistic within approximately ten years. It assumes an AEC efficiency of about 70% and is mainly in line with the short term optimistic scenario but with a slightly lower overall material and energy demand.

6. Medium term optimistic scenario (MT-O)
   A favourable technology landscape (i.e. better electrodes, efficient cost optimisation) is captured in the medium term optimistic scenario. It features a very optimistic AEC efficiency of 75% and a low energy demand due to heat integration between the methanol reactor and the distillation unit. The material demand is the lowest and the DAC sorbent cocktail has been optimised significantly with a lifetime of approximately 8 years (48.000 hours).

These scenarios aim to describe the potential future states of the microplant. The technical background can be found in the ex-ante life cycle inventory chapter, the implication of using these scenarios is discussed in the limitations section.

3.4.4. System boundaries and functional unit

A cradle-to-gate system boundary and a temporary carbon credit of -1 kg CO_2 eq. / kg CO_2 captured
The introduction explained how methanol and derived DME form the basis for a variety of fuels and materials that can be used in a wide range of (manufacturing) processes. In other words, methanol provides many services across industries and sectors. The versatility of methanol complicates the definition of a single functional unit and with it the identification of a use and end-of-life process to capture the full life-cycle impacts of methanol. Considering that this project studies a system that will be implemented in a future scenario, the range of services becomes even greater, as it is currently unknown which specific markets the ZEF methanol will cater for when operational. The guidelines on Life Cycle Assessment of CCUS technologies by Ramírez Ramírez et al. (2020) and Müller et al. (2019) both state that preferably, the full life cycle of the products (i.e. cradle-to-grave) produced by a CCU process should be taken into account. Yet, both guidelines also state that when a product is chemically identical to the incumbent or alternative technology, and when it provides the same services, a cradle-to-gate approach can also be justified. Additionally, the focus of this project is at the production of methanol and not its use. For the sake of project manageability, and to allow a more general discussion with an emphasis on the impacts of the methanol produced by the ZEF concept, it is therefore chosen to limit the system boundaries to a cradle-to-gate system. The implications of opting for the cradle-to-gate system boundaries are elaborated in the discussion chapter.
One important methodological consideration for CCU products that make use of carbon dioxide from emitting point sources is the allocation procedure where a choice is made about the allocation of the impacts of the upstream chain of the carbon dioxide feedstock over the emitting and using product system (Ramírez Ramírez et al., 2020). Again, these considerations are less relevant to cases of Direct Air Capture, as CO_2 can be considered to be 'freely' present in the atmosphere without a further upstream chain. In this report, the capture of CO_2 by the DAC is considered a *temporary* carbon sequestration process, coupled to a *negative* emission of -1.0 kg CO_2 equivalent per kg of captured CO_2.

Functional unit: 1kg of methanol
The guidelines by Ramírez Ramírez et al. (2020) and Müller et al. (2019) set apart a number of options for defining the functional unit of CCU products depending on which function the CCU product provides. Methanol, as produced by ZEF BV, is a bulk chemical that will be sold to industrial partners. It is introduced in a mature market that already contains numerous end uses for the product and besides a higher purity, it shares all properties with fossil-based methanol. It is therefore deemed suitable to consider a mass-based functional unit that is typically recommended for chemical products. In this LCA, this results in the following FU: *'The production of one kilogram of methanol at factory gate'.*

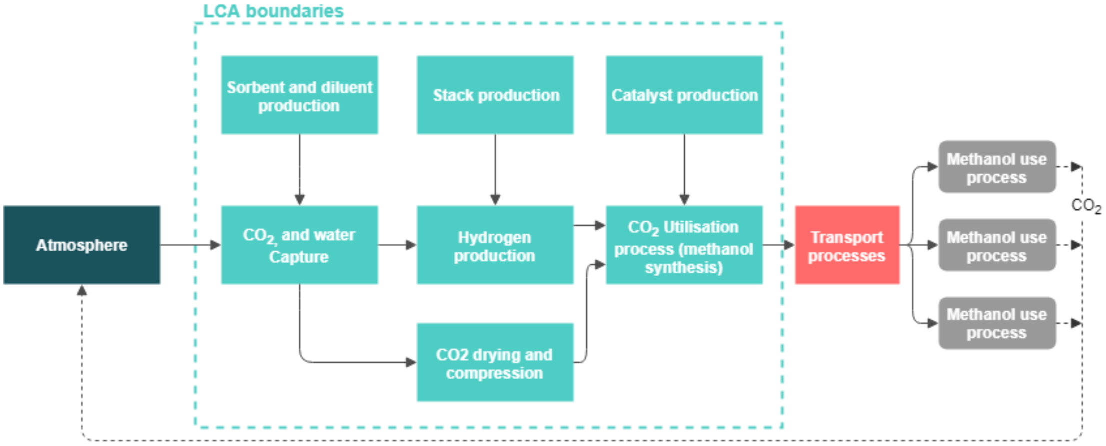


Figure 5: Simplified system boundaries

3.4.5. LCA Flow diagram

Figure 6 provides an overview of the architecture of the LCA model in more detail. The production of some of the more important consumables and parts are modelled in the foreground system. Examples are the production of the sorbent and diluent for the Direct Air Capture unit, the production of the stack for the AEC unit, and the production of the catalyst for the MSR subsystem.
Each individual block in the figure stands for a modelled activity with the exception of the treatment processes. The PV system and the MeOH farm will have their own LCA flow diagrams that can be viewed in the LCI chapter.

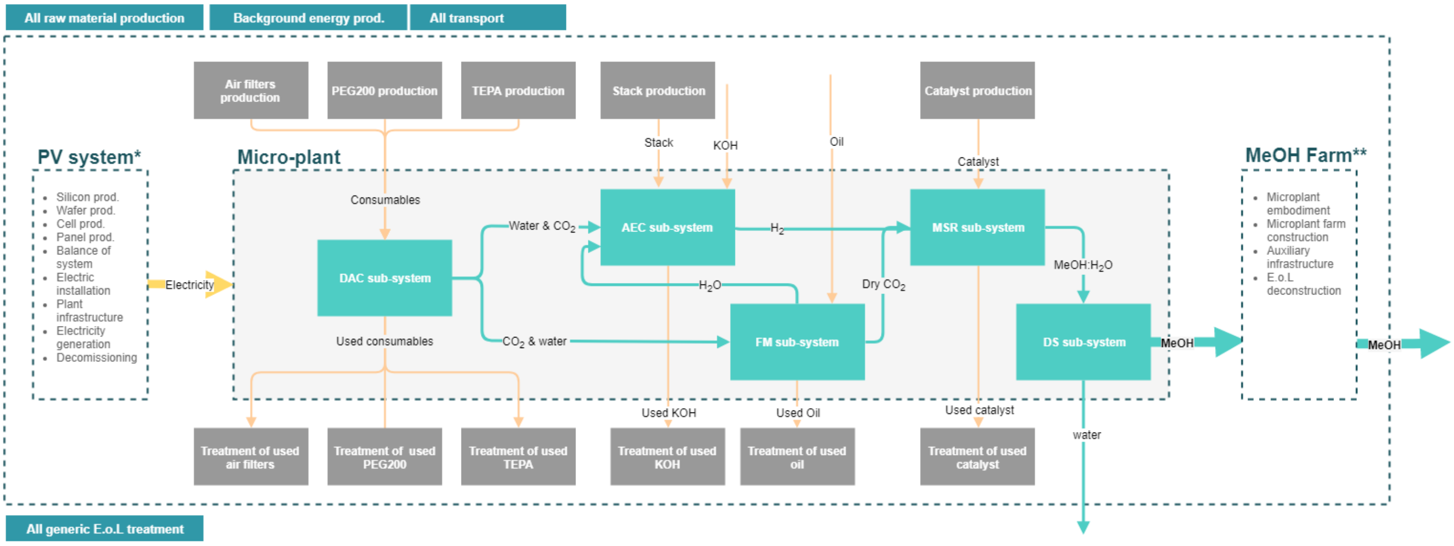


*Figure 6: Full system boundaries of the LCA model. *PV system and **MeOH farm have their individual flow diagrams*

3.4.6. Reference system

Natural gas based methanol from ecoinvent as alternative
Life Cycle Assessments typically combine the assessment of the technology with an additional assessment of the current incumbent or conventional technology to provide a reference for the interpretation of the impact results. Multiple types of reference systems can be envisioned for this project but it is chosen to opt for natural gas-based methanol as opposed to global average methanol production. The low-impurity, high hydrogen/carbon ratio natural gas, requires far less energy for separation and syngas conditioning (IRENA , 2021). It is expected that due to these obvious advantages coal-based methanol will be largely phased out for the European market in the next decade, a natural-gas based alternative therefore might better represent the future market mix.
The reference system should be modelled with the same precision as the assessed technology as to prevent the drawing of incorrect conclusions resulting from aspects that might be modelled in one of the inventories and not in the other. For this study, the ecoinvent dataset for natural-gas based methanol is chosen as opposed to modelling it in the foreground with the most up-to-date data from recent literature. This is done mostly for the sake of effective time management but also to ensure a level of consistency with comparable studies. Ecoinvent maintains relatively extensive datasets for methanol production. The used datasets originates from 2007 (Althaus et al., 2007) and includes all energy and material needs for the reforming process, a synthesis process and a purification process. This includes material needs for catalyst production and general infrastructure.

Technological improvements in the reference system beyond the background system are excluded
As addressed in the ex-ante literature review, a mismatch between the temporal aspects of the assessed technology and the reference system frequently occurs in LCA studies, leading to a perhaps too optimistic view on the performance of the emerging technology in relation to the incumbent technology.
Although methanol production is a mature technology, some additional improvements can be expected. One of the most impacting processes of NG-based methanol production is the combustion of a share of the feedstock

gas to sustain the produce heat for all processes (roughly 9-17 MJ of the total 29-37MJ). This heating demand can be replaced by electrical heating, reducing combustion-related direct emissions. Alternatively, carbon dioxide can be captured from the direct emissions after which it can be injected into the synthesis loop to boost production (IRENA, 2021).

The first option, electrical heating, is not too realistic on the short term for high-temperature processes such as NG-based methanol production (Schüwer & Schneider, 2018). The second option, to capture carbon dioxide for further use in the same production chain or a parallel CO_2-based methanol system, is already applied in practice (IRENA, 2021). Only one study detailing this process could be found (Chen, Lu & Banares-Alcantara, 2019). Because data regarding these processes is lacking, and because it is unlikely that these processes will truly reflect the global market in five and ten years, it is deemed acceptable to not include any technological developments in the reference system. In this study, small changes in the impacts of natural gas based methanol are merely the result of the background scenarios. The flipside of not modelling the foreground of the reference system, is that any conclusions in favour of the microplant that stem from its comparison with NG-based methanol are prone to being optimistic.

3.5. *Cross-study analysis*

To answer the final sub-question, a comparison of sorts need to be performed between the environmental performance of the microplant and similar technologies. In this study, a cross-study analysis is used as main method.

3.5.1. Comparing LCA studies

The various approaches to LCA comparison

One would be excused for thinking that due to the large amount of published literature on CO_2 conversion to value-added products, the environmental assessments would not lag far behind. Although it is true that many environmental studies on this subject have indeed been published, there seem to remain plenty of sources for variation. Meunier et al. (2020) observe that although the direct use of carbon dioxide for methanol synthesis has been studied extensively, the exact data for the chemical equilibrium and kinetic constants still differ per study. Coupled to the already existing challenge of comparing environmental assessments as result of varying methodological choices, the comparison of emerging CO_2 utilisation technologies remains challenging. For this reason it will likely prove useful to provide a comparison not based on only a single study or a alternative modelled foreground system, but on the comparison of multiple published LCA studies.

Comparison in LCA forms the basis of understanding the impact results by placing the assessed technology in perspective to an alternative technology. In most cases, LCA practitioners opt for the foreground modelling of the alternative or for the consulting of pre-modelled background databases. However, when the number of potential alternatives is high due to the emerging state of the main assessed technology, the foreground modelling of all alternatives becomes an increasingly complex and mostly a time-consuming task. LCA practitioners therefore sometimes opt for other means of comparison. One of the most well-known methods is LCA harmonization, a procedure where LCA studies with public LCI datasets are aggregated and re-modelled using uniform methodological assumptions. The result is a single or a couple of alternatives that are based on the data collection work by previous LCA authors. These alternatives provide a fairer assessment because they use the same background databases and follow the same assumptions and methodological choices. Examples of harmonization studies for the case of CO_2 utilisation can be found in the work by Artz et al. (2018) and Thonemann (2020) who based their harmonized LCAs on 8 and 13 earlier studies respectively. The disadvantage of harmonization is that it is still time-intensive when the amount of the consulted studies is high. Hung et al. (2020) proposed an alternative technology called 'LiSeT', focused at screening LCA literature to rapidly compare emerging technologies on a number of predetermined key performance indicators. In essence, the method relies on the decomposition of key performance data found in literature, the translation of this data into 'lifecycle aspects', and a structured qualitative/semi-quantitative evaluation resulting in a performance matrix. By doing so it provides a tool for the comparison of multiple technologies while saving time for the practitioner. Some authors apply similar methods by identifying core features of technologies that primarily determine the impact results. Rapid assessment can then 'cut corners' by calculating indicators from these core features that can be compared in a quantitative matrix (e.g. Philis et al., 2019). The disadvantages of both the LiSeT technology and the comparison on basis of calculated indicators, is that it does not allow the calculation of more complex indicators that are specifically important for CO_2 utilisation processes, namely the total climate change impacts.

Cross study analysis

In this study, the comparison will instead be performed via a structured cross-study analysis as previously shown effective by e.g. Garcia-Garcia et al. (2020). Cross-study analysis of LCA literature is not bound to a specific methodology, instead existing reviews are taken as an example. This analysis attempts to review the most recent and relevant literature on low-carbon methanol production to eventually fuel a discussion on the relation of the Z.E.F. microplant concept with its competitors. Special attention will be given to the comparison of the impact results. However, the comparability of LCIA results is highly questionable due to large deviations between studies on a system level (methodology, assumptions), technical level (data collection, completeness), and product level (value chain assumptions and choices). A part of the analytical procedure in the cross-study analysis is to map and tabulate the differences between the reviewed studies on each of these levels. Though it may not be possible to explain all differences between results using this approach, it is expected that it will positively influence the discussion.

3.5.2. Article collection

An initial scoping search was performed to gain an understanding of the technology landscape of methanol production. The search predominantly relied on data collection and insights from the Renewable Methanol report which was published in early 2021 by the International Renewable Energy Agency (IRENA) and the Methanol institute. Using the project finder tool from the Methanol Institute, an overview was made of planned, developing and installed projects that aim to produce methanol either from biomass feedstocks or from captured CO_2 and renewably produced hydrogen. The names and technologies used in these projects were then used to guide the literature search.

Article identification was done via online search engines for literature repositories including Google Scholar, Scopus, Science Direct and Web of Science. The primary selection was performed using keywords in a combination of the following strings: “Life Cycle assessment”, “LCA”, “Environmental assessment”, “E-methanol”, “Renewable methanol”, “low-carbon methanol”, “direct hydrogenation”, “CO_2 reduction”, “biomethanol”, “CCU/CCUS”.

Both forward and backward snowballing was used to find relevant studies that might be excluded from search results due to a mismatch in the search query, a lack of inclusion in the database, or a mismatch in the publication date. Peer-reviewed papers were given the highest priority and industry-based LCA studies were only included if proper reviewing processes were followed.

It should be noted that especially e-methanol is essentially a combination of three technological product systems, namely carbon capture, hydrogen production, and methanol synthesis. Separately, each of these technological systems has been studied extensively by the global LCA community, resulting studies could in theory be combined to form product systems to be assessed in this review. Yet, the vast variety within these product systems would introduce a large amount of variables which transcends the scope of this review. A literature selection is therefore made biased towards the LCA studies that include the entire methanol production chain.

Secondary selection concentrated on those articles that contained a clear discussion on methodological choices and generally showcased transparency in the Life Cycle Inventory.

In addition, a preference was given to studies which showed original content, defined as unique and case-specific data collection, calculation, and communication. Studies not following the ISO guidelines for LCA were exempt from the collection and only included for discussion purposes when other data was lacking.

04

Life Cycle Inventory

1. The photovoltaic system
2. The DAC system
3. The Alkaline Electrolysis Cell
4. Fluid mechanics, Methanol synthesis, Distillation
5. DAC sorbent and diluent
6. Sorbent emissions
7. Microplant embodiment, maintenance, farm construction

4. Life Cycle Inventory

The complete inventory that makes up the LCA model of the microplant in its farm setting is composed of multiple major components. In this chapter, these main components are discussed separately, providing explanations for assumptions and data wherever necessary. The first section details the photovoltaic system, the second motivates the LCI of the microplant.

The microplant inventory almost entirely relies on data from Z.E.F.
It is inherent to the case-specific and low TRL nature of this research project that data is scarce and uncertain. All data detailing the operation of the microplant is provided by Z.E.F. and is mostly based on preliminary calculations and estimations based on literature. Only in some cases is data backed by experimental findings of early prototypes. It should be clear that this results in a low overall certainty that can only partially be mitigated using the scenario approach. Any reader of this study is advised to take this into consideration.

4.1. *The photovoltaic system*

4.1.1. Panel type

All energy needs of the array of microplants are supplied by a photovoltaic plant consisting of bifacial single-crystalline panels. The panels are assumed to use cells with a passivated emitter and rear cell (PERC) architecture (Jiu et al., 2021). These assumptions are in line with the most up to date plant design offered by the main partner of ZEF BV at the time of writing. A detailed overview of the panel types can be found in appendix J..

4.1.2. Updated PV LCI

Datasets of the ecoinvent database are too outdated for this study
In the first LCA iteration the photovoltaic system seemed to account for over 50% of the climate change impacts of the microplant. This initial iteration made use of the photovoltaic inventory in the ecoinvent 3.7. database. However, even in this most recent version of the ecoinvent database the inventories for photovoltaic systems seem outdated for a rapidly advancing technology such as photovoltaics. Other downstream processes in the database such as the energy and material requirements for the Balance of System (i.e. the mounting system), wiring, and the PV plant construction were modelled for small-scale plants of around 570kW, which is much smaller than the plant that will deliver electricity to the microplant farm. A last remark to the inventories as included in ecoinvent is that no plant inventories are available for Single-crystalline (or single-Si) plants.
To accurately model the impacts of the microplant the LCI for the PV installation therefore needs to be re-modelled using the best available data.

Main data source: The IEA's PV life cycle inventories
The updated version of the photovoltaic system in this report is a new LCI dataset that describes the photovoltaic system that will deliver the electricity for the Z.E.F. methanol plant. It is mostly composed of newer LCI datasets from the International Energy Agency's Photovoltaic Power Systems programme (IEA PVPS). Under the task 12 work package an international collaboration of PV manufacturers and LCA experts work together to compile environmental profiles of currently available PV technologies. This LCA uses the 2020 outcomes of the task 12 work-package which is composed of a set of life cycle inventories for major PV technologies, including single-crystalline silicon PV panels (Frischknecht et al., 2020). The IEA PVPS task 12 LCI dataset is based on the recycled content approach and should be combined with the corresponding life cycle inventories for PV module recycling (Frischknecht et al., 2020). For an elaboration on recycling in LCA the reader is referred to the discussion.

4.1.3. Data collection & manipulation

In all upstream processes from the point of PV panel production (i.e. silicon & wafer production) the IEA PVPS task 12 is copied to this project with only once exception. The activity that is not included in this LCI is the Chinese market mix of photovoltaic grade silicon. According to the authors of the task 12 LCI dataset, the market mix for photovoltaic grade silicon is composed for 61% of silicon from Chinese origin, 16.2% from

Oceanic origin, 13.5% European origin, and 9.28% American origin. In an interview with the supplier of the PV plant it became clear that most of the silicon is produced in China (personal communication, n.d.). It is therefore assumed that the Chinese market mix consists for 100% of Chinese photovoltaic grade silicon.

4.1.4. Bifacial panels

A more important transformation of data from the task 12 LCI is needed for the panel production process. The task 12 dataset merely considers the production of monofacial panels while the panels that will be used in the microplant farm configuration will most likely be bifacial (H. Jongebreur, personal communication, n.d.). The efficiencies, power output, lifetimes, and material requirements differ significantly between these two types and should therefore be modelled accordingly. Most of the data requirements could be collected from an interview with the PV supplier, received data was then checked with data from Jia et al. (2021) who published a paper on the LCA of various PV technologies, including bifacial single-Si panels. Additionally, if data from the task 12 LCI was deemed relatively outdated, it was supplemented by data from Méndez et al. (2021) who recently published a detailed comparative LCA on a novel type of silicon production a including detailed LCI for panel production.

The most relevant data transformation steps were the removal of the backsheet from the task 12 dataset and replacement by solar glass and the reduction of aluminium in the frame of the panels. Jiu et al. (2021) explain that bifacial panels can be dual-glass encapsulation or transparent back sheet encapsulation. In collaboration with the employee from Z.E.F.'s PV supplier it was chosen to opt for the dual glass architecture as this was expected to best represent the panels sold by the manufacturer. To enlarge the illuminated surface on the back of the panel the aluminium bevel is typically smaller than for monofacial panels (CHINT solar, personal communication). It was assumed that this results in a 10% overall aluminium input reduction. The combined LCI for panel production can be found in appendix K.

4.1.5. Mounting system

The balance of system includes all material and energy inputs required for the positioning of the solar panel in the desired configuration. Again a combination of data from Frischknecht et al., (2020), Méndez et al. (2021), and the interview with the PV supplier result in an aggregated inventory. Balance of system components strongly differ per manufacturer and even differ per project of the same manufacturer. The interview with the PV supplier therefore was deemed most valuable, in combination with the data from Méndez and colleagues. Contrary to the task 12 dataset no concrete foundation was modelled for in this LCI as it is assumed that steel poles are driven deeper into the ground instead (CHINT solar, personal communication, n.d.).

4.1.6. Electric installation

Both the newer IEA PVPS task 12 LCI dataset and the 3.7.1. ecoinvent database provide a LCI for the electric installation needed for a larger scale PV plant which represent the requirements for the fuse box, electric cables, and the electric meter. As provided, the largest plant that is represented by the dataset has a capacity of 1.3 MWp which much smaller than the proposed plants by CHINT solar. Unfortunately, the datasets are not transparent in the assumptions made for the scaling of the data between the plant sizes, which makes linear scaling questionable. Instead the data from Méndez et al. is used as it represents the most up to date real life bill of materials for PV plant construction. Some scaling is applied to scale back the LCI from the 50MW installation as described by Méndez et al. to the 14 MW installation for the microplant. The scaling exercise was double checked with the PV supplier and deemed suitable.

Direct integration of the microplant in the PV system eliminates the need for PV-side inverters

Normally, inverters are an integral part of the LCI of PV systems to convert the variable direct current of the panels to the alternating current matching the requirements of the grid. This is not required for the microplant-solar-farm as each microplant features its own inverter as part of its direct integration capabilities. The inverter is therefore not included in this LCI. The demand of the electric installation will also be smaller because of the reduced need for interconnection between panel arrays and the lack of a grid connection. Still, because there remains uncertainty about the internal wiring demand of the microplant-solar-farm and to prevent underestimation of impacts, the electric installation is still taken into account in this LCI following the dataset by Méndez et al.

4.1.7. Plant construction & performance

The plant performance was modelled by the PV supplier using dedicated PV modelling software as recommended by the IEA PVPS guidelines for the life cycle assessment of LCAs (Frischknecht et al., 2016). The total average performance of the modules in four potential locations is aggregated in table 1.

Table 1: PV plant capacity and amount of panels required to deliver ~34.7 GWh per year for methanol production via 3250-4000 microplants.

	Salalah Freezone	Dhofar governorate	Sohar	Al Buraymi governorate
Capacity (mw)	14.18	13.21	14.35	13.86
Panels (units)	27200	25400	27600	26700

The PV modelling software includes all sorts effects such as weather and albedo effects. As can be seen in the table the required amount of panels of 1.6m2 differs slightly per location due to variances in solar irradiation and local conditions.

PV modules degrade over time which reduces the total efficiency of a PV plant. The IEA PVPS task 12 guidelines (2020) recommend an annual linear degradation rate of 0.7%. However, the panels provided by CHINT solar come with a 30 year warranty for Extra Linear Power Output
(1st year ≤ 2.0%, 2nd to 30th years ≤ 0.45% / year). Over the 30 year lifetime, this results in an average total decrease of power output of 6.613%. To simulate the degradation, the electricity production activity in the LCA model considers the total lifetime of the PV plant and subjects the power output of the first year to a 6.525% penalty. Overall lifetimes were assumed to be 30 years, as assumed by Jia et al (2021) and recommended by the PV supplier.

4.2. *The DAC system*

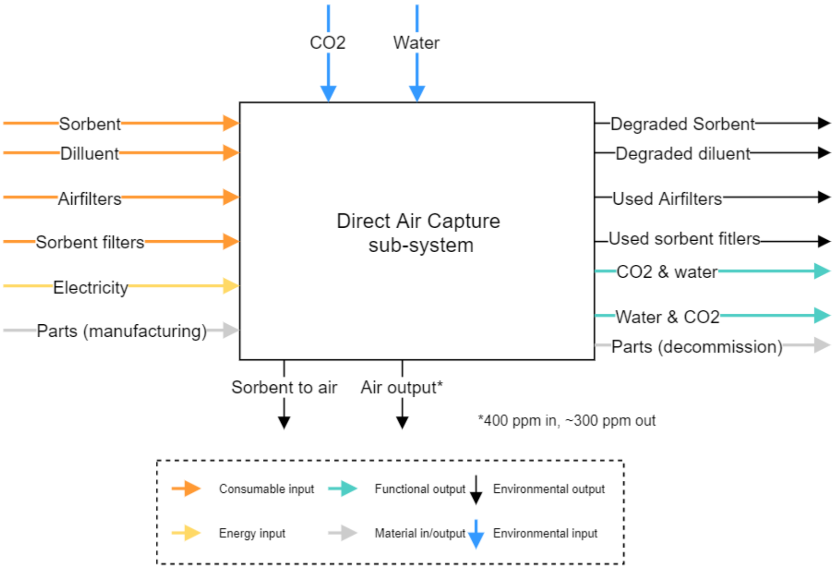


Figure 7: Schematic overview of the environmental and economic flows into and out of the Direct Air Capture system.

4.2.1. Energy requirements

In recent LCA literature (e.g. Sternberg et al., 2017, Rosental et al., 2020) the large energy requirements for the desorption of CO_2 and internal recycling of adsorbing materials is regarded as the main factor that severely limits the efficiency and thereby promise of DAC – CCU combined systems. Indeed, also for the Z.E.F. microplant system the DAC is responsible significant portion of the energy demand.

The energy inputs of the DAC LCI consists of data provided by the technology developers at Z.E.F. B.V. The collected data is based on preliminary lab-scale results of a smaller-sized DAC unit. The data was then transformed to the minimal requirements for the economically feasible operation of the DAC system. This transformation, albeit in part subjective, was performed while taking into account the upper and lower bounds of the performance limits. The upper bound (i.e. most efficient) energy use can be determined by calculating the amount of energy needed for the *thermochemical* desorption of CO_2 from the sorbent according to the formula for the specific heat capacity.

$$Q = c \cdot m \cdot \Delta T$$

Where c is the specific heat capacity of the loaded sorbent, m is the mass of the sorbent, and ΔT is the change in temperature from the initial temperature of the sorbent to the point where it re-releases the captured CO_2 and H_2O. Although well-insulated, the system suffers from thermal losses. To increase the efficiency of the heating elements a heat exchanger is placed in the sorbent circulation loop. Both the thermal losses and the efficiency of the heat exchanger then determine the overall energy required for the desorption phase. Current lab-scale results hover around an energy requirement of 400kj/mol of CO_2 to maintain a temperature of between 100-120 degrees Celsius in the desorber column. Other energy requirements originate from the operation of the fans for the air inlet and the pump to recycle the sorbent.

The current LCI for the DAC unit represents a single mode of operation and many factors can change the process parameters (M. Singha, personal communication, n.d.). Regardless, it is expected that the approach to the LCI is sufficiently realistic, for deeper analysis the reader is nevertheless advised to compare the results with the most recent literature on Direct Air Capture at the time of reading.

Similarly, the energy input for the DAC unit as received by the technology developers was compared to the work by Deutz & Bardow, who published a LCA study on the DAC unit as developed at Climeworks (Deutz & Bardow, 2021). Although the Climeworks DAC unit is batch operated and consists of larger units, its normalised energy requirements (kWh/kg CO_2) should fall within the same range. Deutz & Bardow also engaged in discussions with the technology developers at Climeworks to establish realistic future targets for the technology. The resulting overview in comparison with the energy requirements reported by ZEF are shown in table n.d. It can be observed that compared to the data reported by Climeworks, the Climeworks DAC unit seems to perform better in terms of energy demand. Potential sources for the performance difference are probably the result of the more mature technological state of the Climeworks model, which has benefitted from a long research trajectory. Regardless, the energy demand reported by ZEF seems to be in a realistic range.

	CW- Today	CW- Future	ZEF-Today	ZEF-Future	Unit
Electricity	0.7	0.5	3.6	2.9	kWh/kg CO_2
Waste heat	3.3	1.5	-	-	kWh/kg CO_2
Heat pump	1.3	0.6	-	-	kWh/kg CO_2
Total (waste heat version)	5.0	2.0	-	-	kWh/kg CO_2
Total (elect. version)	2.0	1.1	3.6	2.9	kWh/kg CO_2

Table 2: Performance of the DAC unit from Climeworks as reported by Deutz & Bardow (2021) in comparison to the energy demand of the ZEF DAC unit.. The Climeworks DAC system has two versions; one running on waste heat, the other on a heat pump, hence the different total energy demand.

4.2.2. Material exchanges

To produce around 2000 grams of methanol per day under 8 hours of operation, the DAC unit should capture an amount of CO_2 according to the following equilibrium reaction:

$$CO_2 + H_2 \rightleftharpoons CH_3OH + H_2O$$

Accounting for some losses in the separation of the water:CO_2 mixture and in the methanol reactor, the amount of CO_2 captures should be around 2750grams per day. The total mass balance of the CO_2 within the system will be elaborated later.

To estimate the material requirements for the production of the DAC unit estimations are used from Z.E.F., based on an updated CAD model of the DAC and resulting bill of materials. The full B.O.M. is not included in this study due to its proprietary nature. Instead, the various parts are aggregated into single material inputs. The combined result of both the material and energy exchanges can be viewed in table 3.
The LCI for the manufacturing of the DAC unit is composed of raw material input only, manufacturing processes such as injection moulding, sheet rolling, machining, etc. are not taken into account in this research project due to its low relative influence on the impact results. The table details the unit process data for the co-capture of 1 kg of CO_2 and 1.23 kg of H_2O, as is currently the case in the microplant system.

Table 3 Unit process data for the ***co-capture*** *of 1kg of* CO_2 *and co-capture of 1.23 kg of* H_2O*. LCI data is indicative for the ST – N scenario, the full LCI is parameterized and cannot be viewed in this report*

Flow Type	Product / emission	amount	Unit	Parameters
Environmental flow (emission)	Ammonia	4.74E-05	Kg	Sorbent lifetime NH3 emission rate
Environmental flow (sequestration)	Carbon dioxide, to soil or biomass stock	-1.0	Kg	
Product	DAC subsystem – MF – capture of carbon dioxide and water from ambient air	1	Unit	Functional output
Economic flow: (Foreground)	Sorbent	0.000592	Kg	Sorbent lifetime
Economic flow: (Foreground)	Diluent	0.000592	Kg	Diluent lifetime
Economic flow: (Foreground)	Electricity from PV	3.6	kWh	DAC energy demand
Economic flow (Background)	flat glass, coated	0.000502	Kg	Microplant lifetime
Economic flow (Background)	transport, freight, sea, container ship	0.012859	Ton/km	Sorbent lifetime Microplant lifetime
Economic flow (Background)	waste mineral wool	-2.4E-05	kg	Microplant lifetime
Economic flow: (Foreground)	polyester fibre, finished, adapted from ecoinvent	0.000947	kg	Microplant lifetime
Economic flow: (Foreground)	polypropylene, granulate	0.000304	kg	Microplant lifetime
Economic flow: (Foreground)	steel, 316	2.61E-05	kg	Microplant lifetime
Economic flow (Background)	stone wool production	2.37E-05	kg	Microplant lifetime
Economic flow (Background)	transport, freight, lorry 16-32 metric ton, EURO5	3.55E-05	Ton/km	Sorbent lifetime Microplant lifetime
Economic flow (Background)	transport, freight, lorry >32 metric ton, EURO6	0.001123	Ton/km	Sorbent lifetime Microplant lifetime
Economic flow (Background)	waste glass, municipal incineration	-5E-05	kg	Microplant lifetime
Economic flow (Background)	waste plastic, mixture, municipal incineration	-0.00095	kg	Microplant lifetime
Economic flow (Background)	waste polypropylene, municipal incineration	-0.0003	kg	Microplant lifetime

4.3. *The Alkaline Electrolysis Cell*

LCA studies on CO_2-based methanol typically include the production of hydrogen within the system boundaries. In most of these papers hydrogen production is then cited as the most relevant contributing factor for most impact categories, for examples see the cross-study analysis. The microplant design includes a small alkaline electrolysis cell to supply the methanol reactor with enough hydrogen to produce about 2000 grams of methanol per day. The electrolyser is composed of a stack of cells that are compressed to withstand the high pressure environment (around 50 bar) in the AEC. Each individual cell consists of multiple layers, including a bipolar plate made of nickel, inner boundary layers, the electrodes, the membrane, and o-rings.

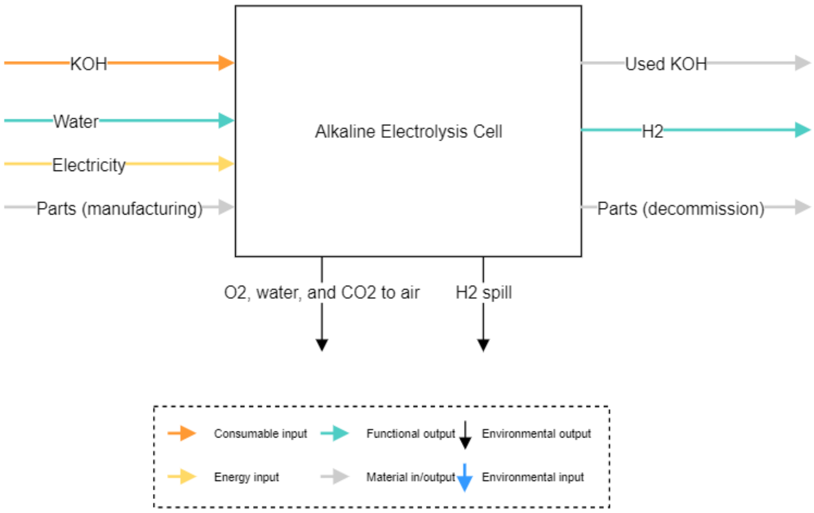


Figure 8: Schematic overview of the environmental and economic flows into and out of the Alkaline Electrolysis Cell subsystem

4.3.1. Energy requirements

In practice, overall efficiencies of around 75% can be typically reached in alkaline electrolysers. The efficiency of operation in the case of the microplant is relatively simple. The more voltage is applied to the stack the higher the overall efficiency. Furthermore, the current density in the stack also determines the power input and is closely linked to the overall efficiency. If for example, the amount of cells in the AEC unit is doubled, the current density can be halved, resulting in a 10% increase in efficiency. Both the amount of cells and the voltage applied to the system are important technological considerations. The ZEF technology developers make these choices mainly based on cost considerations to keep the overall cost of the microplant within a target range.

The current lab-scale AEC unit achieves an efficiency of 61%. However, in the most up to date iteration of the microplant design the AEC is assumed to be composed of 120 cells with a total current density of 0.2 A / cm^2. This results in an average efficiency of 68-70%. This average efficiency is used to calculate the total energy demand required for the production of enough hydrogen to produce around 2kgs of methanol per day which comes to 0.38 kg H_2 per day. Under the ST-N scenario, the total amount of electricity required to achieve this production target is 18.0 kWh per day.

To validate these values the total energy input is compared to the LCI provided by Delpierre and colleagues (2021) in their ex-ante LCA of hydrogen production in the Netherlands. The authors found that for 2019 average consumption of electricity is around 50 kWh / kg H_2, towards 2050 electricity consumption can be expected to decrease to 47 kWh / kg H_2. The electricity consumption of the AEC in this study falls within this range with 47.5 kWh / kg H_2 respectively. Variations in the electricity demand and overall structure of the AEC unit will be elaborated in the ex-ante LCI.

4.3.2. Material requirements

The integrated microplant system has as key benefit that ultra pure water required for the production of hydrogen is captured in the DAC unit. Contrary to many other CO_2-based methanol production systems, there is no need for the distillation or purchase of highly pure water, omitting part of related impacts.
The other most important material inputs for the AEC system originate from the production of the AEC stack which is composed of individual AEC cells. As previously explained these cells are made up of a bipolar plate made of nickel, inner boundary layers made of polysulfone (PSU), the electrodes, the membrane, and materials for the enclosure of the cells in the stack.

Under the ST-N scenario the electrodes are assumed to be made of bare-nickel, a cheap option for the production of electrodes with long lifetimes. Other scenarios consider Raney-nickel electrodes or DLR electrodes, as will be explained in the ex-ante LCI chapter. The number of cells in the stack is determined using an excel workbook that calculates the required number of cells based on the ratio between the peak power per cell (a function of the current density, cell area, and stack voltage) and the overall peak power needed by the AEC.

The membrane in the AEC cells is assumed to be a Zirfon membrane, developed by the Afga-Gevaert group. The Zirfron membrane roughly contains 80wt% zirconiumoxide and 15wt% polysulfone in an encasing of 5wt% polyphenylene sulfine (PPS). The membrane is assumed to merely consist of these materials and the energy demand for the manufacturing of both the membrane and the cells is not considered in this LCI.

The typical electrolyte used in AEC cells is potassium hydroxide (KOH). The AEC is assumed to contain around 5 kgs of KOH, the 'consumption rate' or lifetime of the electrolyte is assumed to be around 8 years under an average of 7 hours of operation per day at an OEE of 97%. Over the full lifetime of the AEC, this coincides with averages from literature which range between 1-2 gr / kg H_2 (Noack et al., 2015).

The lifetime of the stack is an important KPI and will likely follow industry average lifetimes
The lifetime of the stack is one of the more important parameters of the microplant as a short lifetime could make the entire project financially unattractive (J., van Kranendonk, personal communication, n.d.). Additionally, from an environmental perspective shorter lifetimes would be detrimental due to the required additional input of high impact materials such as nickel. Under the default ST-N assumptions the stack lifetime is approximately 60.000 hours, which is slightly below the average industry stack lifetime of 75.000 hours (Perrin et al., 2021). A lifetime of 60.000 hours is about 20 years of operation considering that the AEC only runs when it receives electricity from the photovoltaic panels.
Other assumptions are elaborated in the ex-ante LCI chapter. The combined LCI for the AEC unit can be viewed in table 4 and 5.

Table 4: Unit process data of the Alkaline Electrolysis Cell for the production of 1 kg of hydrogen

Type	Product / emission	amount	Unit	Parameters
Environmental flow (emission	Carbon dioxide	4.74E-05	Kg	Sorbent lifetime NH3 emission rate
Environmental flow (emission	Water	2.4E-4	Kg	
Product	Hydrogen	1	kg	Functional output
Economic flow (foreground)	AEC stack production	3.5E-4	Kg	Stack lifetime
Economic flow (foreground)	Water from DAC subsystem	0.000592	Kg	
Economic flow (Background)	ceramic tile production	6.91E-5	kg	Microplant lifetime
Economic flow (foreground)	electricity production, photovoltaic, open ground installation	47.5	kWh	AEC energy demand

Economic flow (Background)	inverter production, 2.5kW	3.5E-4	unit	Microplant lifetime
Economic flow (Background)	market for transport, freight, sea, container ship	9.3E-2	Tons/km	Electrolyte lifetime
Economic flow (foreground)	market group for waste polypropylene	-3.4E-5	kg	Microplant lifetime
Economic flow (foreground)	polypropylene production, granulate	3.4E-5	kg	Microplant lifetime
Economic flow (foreground)	potassium hydroxide production	8.6E-3	kg	Electrolyte lifetime
Economic flow (foreground)	steel production, 316	2.37E-05	kg	Stack lifetime Microplant lifetime
Economic flow (Background)	transport, freight, lorry 16-32 metric ton, EURO5	2.6E-4	Ton/km	Sorbent lifetime Microplant lifetime
Economic flow (Background)	transport, freight, lorry >32 metric ton, EURO6	8.0E-3	Ton/km	Sorbent lifetime Microplant lifetime
Economic flow (Background)	treatment of waste plastic, industrial electronics, municipal incineration with fly ash extraction	-1.0E-4	kg	Microplant lifetime

Table 5: Unit process data for the production of the stack as input for the AEC

Type	Product / emission	amount	Unit	Parameters
Product	AEC stack	1	Unit	
Economic flow (Background)	Polyphenylene Sulfide	0.81675	Kg	Nr. Stack cells
Economic flow (Background)	Polysulfone	8.2924	Kg	Nr. Stack cells
Economic flow (Background)	Synthetic rubber	0.14689	Kg	Nr. Stack cells
Economic flow (Background)	Nickel Class 1	2.541	Kg	Nr. Stack cells
Economic flow (Background)	Zirconium oxide	(…)		
Economic flow (Background)	Waste plastic, mixture	-9.1091	Kg	Stack lifetime

4.4. *Fluid mechanics, methanol synthesis, and distillation*

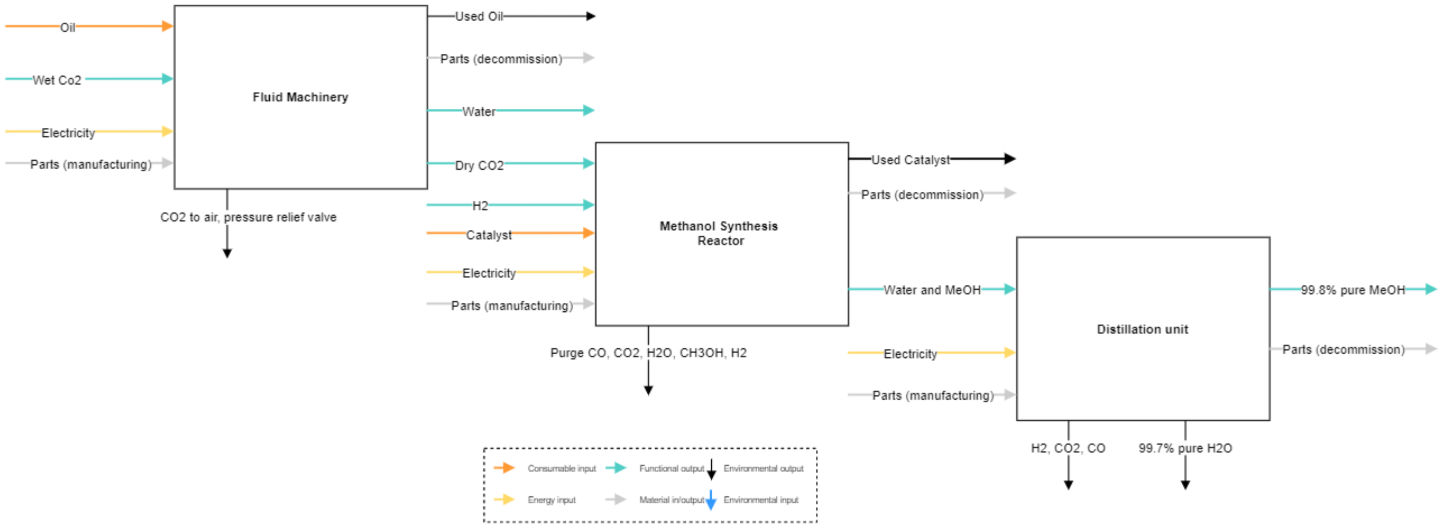


Figure 9: Schematic overview of the environmental and economic flows into and out of the fluid mechanics, methanol system, and distillation subsystems

4.4.1. Fluid machinery

Both energy and material requirements for the fluid machinery subsystem are relatively straightforward. The overall efficiency of the FM system is quite low due to the use of of-the-shelf compressors from refrigeration systems. This however, will likely change and it can be expected that the FM system will see a major leap forward in its energy efficiency. Any changes in the energy demand however, will likely not be relevant on the microplant level as the energy demand for the compression of the carbon dioxide flow from the DAC unit pales in comparison to the energy demand from the AEC. Due to its lower relevance, a validation check with literature is not performed for the FM system.

All material inputs are estimated from the most recent microplant design and mostly consist of steel for all parts, stone wool for the insulation of the entire system, and some aluminium for the valves. Compressor oil is the only consumable used in the FM system and therefore also receives it's own lifetime. It is assumed that the compressor oil is replaced every eight years. Transport movements are implemented in the FM LCI activity for the initial transport of the system to the installation location, its decommissioning, and movements for the replacement of the compressor oil.

4.4.2. Methanol synthesis reactor

As explained in the overview of the microplant, the methanol synthesis reactor is non-conventional in the sense that it is natural convection driven and has the potential to be autothermal.

The latter forms one of the main benefits of this reactor design and entails that the heat released in the exothermic reaction of hydrogen and carbon dioxide into methanol meets the heating needs at the inlet of the reactor for raising the temperature of the hydrogen and carbon dioxide mixture to appropriate levels. Compared to the reactor designs of larger methanol plants, this particular design eliminates the need for additional pumps, auxiliary heat production, and multi-stage reactors. Additionally, its smaller size allows the start-up of the reactor using merely electricity, thus omitting part of the emissions coupled to this stage in larger plants. The methanol reactor still contains some small heating elements subdivided in a pre-heater, a heater of the convection driver, and a heater for the reaction bed. The energy demand of these heating elements is approximately 1.2 kWh per day and is mostly taken up by the initial start-up phase of the reactor each day.

The reactor utilizes a fairly standard catalyst composed of copper, zinc oxide, and aluminium oxide ($Cu/ZnO/Al_2O_3$) that is also seen in most LCAs on CO_2-based methanol (Artz et al., 2018). Because the production of hydrogen tends to primarily determine the environmental profile of CO_2-based methanol, the efficient use (i.e. yield) of this feedstock in the methanol reactor is a crucial performance indicator. Decreases in the activity of the catalysts as result of chemical reactions with the reactor contents therefore form a key technological challenge in the development of CO_2-based methanol systems. To maintain a high yield the catalyst needs to be replaced at set frequencies. Under the standard ST-N scenario the catalyst is expected to be replaced every ten years.

A continuous purge of 2%
To measure the contents of the reactor and to rid the reactor of accumulated nitrogen, the contents are occasionally purged in a magnitude of around 2% of the feedstock gasses. The mixture of CO_2, CO, H_2, H_2O, and trace amounts of MeOH is then released into the atmosphere. In the current design iteration of the microplant these gaseous contents are expelled without flaring, meaning that MeOH is not converted back into CO_2 and H_2O. The exact composition of the purged gasses is assumed to be around 100gr CO_2, 25gr H_2, 19gr CO, and 9.4 gr MeOH per day, based on preliminary calculations provided by ZEF. The purging of gasses from the reactor will also be subjected to a sensitivity analysis.

4.4.3. Distillation system

Because the methanol reactor produces water and methanol in a 1:1 molar ratio, the resulting mixture needs to undergo an additional separation step. The mixture leaves the reactor in a liquid state, so distillation is the default process to separate the two fluids. The distillation sub-system is currently assumed to consist of a distillation column, reboiler, condenser, and a flash distillation column. It closely follows conventional distillation column design but on a smaller scale. Using electric heating elements, the methanol and water are separated with a purity of 99.8% and 99.6% purity respectively. The energy demand under the ST-N scenario is assumed to be 0.75 kWh. This seems to be within range compared to the macro-scale CO_2-based methanol system design by Bos, Kersten & Brilman (2020) who used an average energy demand of around 0.40-0.43 kWh/kg of MeOH output, and the system assessed by Nyari (2018) who designed a similar system with an average energy use of 0.64 kWh per kilogramme of methanol.

Table 6: Unit process data for the carbon dioxide compression (FM) subsystem.

Type	Product / emission	amount	Unit	Parameters
Product	FM subsystem, pressurization of carbon dioxide	1	Unit	
Economic flow (Foreground)	Carbon Dioxide from DAC subsystem	1	kg	
Economic flow (Foreground)	electricity production, photovoltaic	0.33 (ST-N)	kWh	compression energy demand
Economic flow (Background)	market for aluminium, cast alloy	1.90 E-4	Kg	Microplant lifetime
Economic flow (Background)	market for lubricating oil	1.90 E-4	Kg	Lubricating oil lifetime
Economic flow (Background)	market for waste aluminium	-1.90 E-4	Kg	Microplant lifetime
Economic flow (Foreground)	market for waste mineral wool	2.37 E-5	kg	Microplant lifetime
Economic flow (Background)	steel production, 316	4.00 E-5	kg	Microplant lifetime
Economic flow (Background)	stone wool production	2.37 E-5	Kg	Microplant lifetime
Economic flow (Background)	treatment of waste mineral oil, hazardous waste incineration	-1.90 E-4	kg	Microplant lifetime

Table 7: Unit process data for the methanol synthesis subsystem

Type	Product / emission	amount	Unit	Parameters
Product	Methanol water mixture (1 kg of MeOH)	1	Unit	
Environmental flow	Carbon dioxide	5.51 E-2	kg	
Environmental flow	Carbon monoxide	9.74 E-3	Kg	
Environmental flow	Hydrogen	1.30 E-2	Kg	
Environmental flow	Methanol	~9.42 E-3	Kg	
Environmental flow	Water		M3	
Economic flow (Foreground)	AEC subystem, hydrogen production by alkaline electrolysis	0.192	kg	
Economic flow (Foreground)	FM subsystem, pressurization of carbon dioxide	1.41	kg	
Economic flow (Foreground)	MS catalyst - copper zincoxide aluminium oxide	3.52E-5	unit	Catalyst lifetime
Economic flow (Foreground)	electricity production, photovoltaic	0.75 (ST-N)	kWh	Reactor energy demand
Economic flow (Background)	market for waste mineral wool	-3.52 E-5	kg	Microplant lifetime
Economic flow (Background)	steel production, 316	8.67 E-4	Kg	Microplant lifetime
Economic flow (Background)	stone wool production	3.52 E-5	Kg	Microplant lifetime

Table 8: Unit process data for the distillation subsystem

Type	Product / emission	amount	Unit	Parameters
Product	Methanol	1	kg	
Environmental flow	Carbon dioxide	1.20 E-2	kg	
Environmental flow	Carbon monoxide	1.53 E-5	Kg	
Environmental flow	Hydrogen	2.01 E-5	Kg	
Economic flow (Foreground)	Methanol and water mixture	1	Unit (contains 1 kg MeOH)	
Economic flow (Foreground)	electricity production, photovoltaic	0.75 (ST-N)	kWh	Distillation energy demand
Economic flow (Background)	market for waste mineral wool	-3.52 E-5	kg	Microplant lifetime
Economic flow (Background)	market for waste polyethylene/polypropylene product	- 7.04 E-6	Kg	Microplant lifetime
Economic flow (Background)	polypropylene production, granulate	7.04 E-6	Kg	Microplant lifetime
Economic flow (Background)	steel production, 316	2.00 E-5	Kg	Microplant lifetime
Economic flow (Background)	stone wool production	3.52 E-5	kg	Microplant lifetime

4.5. *DAC sorbent and diluent*

4.5.1. Amine based sorbents for CO_2 capture

The amine based capture of CO_2 is currently the most mature technology, mostly due to its cost-effectiveness (Spietz et al., 2020). A typical amine-based capture system consist of an absorption column where the amine sorbent reacts with CO_2 in the gas phase and a desorption column where heat is applied to stimulate a reversible reaction that forces CO_2 out of the sorbent. Mono-ethanolamine is the currently mostly used amine but polyamines have been discovered to offer better absorption for CO_2 (Muchan, 2017, as cited by Dubhashi, 2019).

4.5.2. Choice of amine for the microplant

Various teams at ZEF have analysed the use of liquid amines for the capture of CO_2 in a variety of process designs. In the most recent iterations two types of amines were considered. One of the earlier liquid amines was polyethylenimine (PEI) which can be a linear polymer composed of secondary amines with primary amines at its ends, or a branched polymer of combined primary, secondary, and tertiary amines (Mulder, 2021). During the loading of CO_2 into the amine the compound becomes increasingly more viscous up to a point where the cycling of the sorbent becomes impossible. After repeated experimental testing another amine was proposed; tetraethylenepentamine (TEPA). During testing it was found that compared to PEI TEPA has a higher absorption capacity, better performance in the presence of water, and exhibits less chemical reactions with CO_2 (Mulder, 2021). An important benefit of TEPA is its reduced viscosity compared to PEI under heavy CO_2 loading which enables the cycling of the sorbent.

To potentially improve the CO_2 capacity of the sorbent, a diluent can be added. The diluent of choice for the DAC unit is polyethylene glycol (PEG) due to its high physical solubility of CO_2, which can enhance the mass transfer rates. PEG can be further characterized by its molecular weight which can strongly defer depending on the chain length. The polyether compound used by ZEF is PEG-200.

It is uncertain whether the current amine used as sorbent in the DAC system will be the eventual sorbent used at market introduction. The current compound inhibits some adverse properties such as its thermal instability. Yet, the various types of amines that could be used in the system are part of ongoing research within ZEF. It thus falls outside of the scope of this research to model alternative sorbents.

4.5.3. Production of TEPA and the diluent

Multiple routes of TEPA production are possible but few have detailed data and realistic production methods. In this study a patent from 2018 filed by Ten Kate et al. as part of the R&D by Akzo Nobel will be used to provide reasonably accurate data for the production of TEPA from widely available materials. The yield (efficiency) of this method is relatively low which is why it cannot immediately be assumed that this is the actual process that is used for the production of TEPA in industry. Still the production route provides a basis for inventory modelling using stoichiometry. The initial modelling will be done using the parameters from the patent. A detailed description of the modelling of the sorbent and diluent production process is provided in appendix F.

The energy and heat requirements for the reaction will be based on industry averages as is recommended by Tsoy et al. (2018) in their LCA framework for the upscaling of the production of industrial chemicals. This includes therefore the total energy and heat requirements, including the separation step which is often a highly energy intensive process (Kim & Overcash, 2003). Similar to the inventory modelling by Deutz & Bardow, industry averages will come from the Gendorf Chemiepark which houses the Global Amines company, making it likely that TEPA is produced here. Gendorf publishes core indicators for environmental performance including all average exchanges with the environment (Gendorf, 2020). These averages were compiled, aggregated, normalised, and used as input for the TEPA production process

4.5.4. Sorbent lifetime and end-of-life

The lifetime of the sorbent in the system is determined by its declining cyclic capacity as result of oxidative and thermal degradation. The technology developers stated that the sorbent will likely be replaced as soon as the cyclic capacity has decreased by 20%. In the current lab-scale set-up this level is reached after 6 months of operation. Yet, the developers are optimistic and expect that lifetimes of four years should be possible at market introduction.

4.6. *Sorbent emissions*

Capture emissions are better researched for point source capture than direct air capture but differences should be expected

The use of amines for the capture of CO_2 from the atmosphere or flue gas has been coupled to adverse environmental effects related to both the *evaporation* of the sorbent to the atmosphere and the *degradation* of the sorbent into volatile compounds (Spietz et al., 2020). Due to the relatively high technological maturity most studies of sorbent emissions have been applied to point-source capture systems. It has been reported that the dominant emission product is ammonia but other volatile products that are derivatives of the sorbent in use have been reported as well (Koiwanit, 2014). If ammonia is released to the atmosphere it can either remain in the atmosphere, be transported into the biosphere by winds or washed out of the atmosphere by precipitation into the hydrosphere. Ammonia is toxic to aquatic life, leads to eutrophication of natural areas, and induces acidification in soil (Bobbink et al., 2010). In the atmosphere it furthermore reacts with nitric and sulfuric acid, contributing to the formation of particulate matter (Backes et al., 2016). Other amine-related compounds can also be formed, though the exact nature of these compounds is highly dependent on the type of capture system and local conditions. Some papers report the formation of nitrosamines and nitramines which are highly toxic to human health (e.g. Chen et al., 2018). These are however likely formed by reactions of common pollutants in flue gas with the amines in the capture unit at higher temperatures (Dai et al., 2012). This is therefore not applicable to the case of Direct Air Capture that will more likely showcase thermal/oxidative degradation as opposed to chemical degradation through reactions with pollutants.

Whole evaporation of the sorbent not likely to be impactful

Evaporation of the sorbent leads to emissions of the sorbent in its entirety. The currently preferred sorbent by ZEF is not expected to exist for long in the atmosphere due to degradation by reaction with hydroxyl radicals in the air (Pubchem, n.d.). However, it is unknown what the sorbent will degrade into and it is likely that it will deposit onto surfaces as salts (Pubchem, n.d.). The sorbent in itself is not carcinogenic or toxic but its emissions and atmospheric degradation products may form particulate matter. Gowda (2020) found key influencing factors for the evaporation of the sorbent from the DAC system to be 1) the vapour pressure (i.e. sorbent characteristic, tendency of the molecules to escape from the liquid), 2) The surface area in the adsorber column (i.e. leading to more contact with gasses and resulting evaporation), 3) Temperature (i.e. increasing the kinetic energy of the sorbent molecules), and 4) the flow rate of the gas in the column.

Oxidative and thermal degradation of the sorbent lead to volatile degradation compounds

Degradation of the sorbent produces a wider variety of compounds that can be volatile. The most studied degradation routes are oxidative degradation due to chemical reactions between the amine and oxygen, and thermal degradation which occurs as result of the high temperatures in the stripper column (Spietz et al., 2020). Gowda (2020) furthermore observed that to a smaller extend CO_2 induced degradation and stainless steel induced degradation processes are present in the DAC unit. A part of the degradation compounds will likely be deposited within the system as salts and therefore will never evaporate and leave the system. Although degradation pathways are generally unknown for Direct Air Capture it is expected that ammonia will be the most common degradation product (M., Singha, personal communication, n.d.).

A simplified approach to modelling emissions from sorbent degradation

Unfortunately the exact vaporisation/degradation dynamics remain unknown. It furthermore does not fall within the scope of this study to analyse the exact drivers for evaporation and the resulting impacts. In most recent LCA literature on direct air capture systems emissions from the DAC system are generally not taken into account or even considered (e.g. Rosental et al., 2020; Deutz&Bardow, 2021). LCA studies on point source

capture are a step ahead and sometimes include emissions of MEA (e.g. Eggeman et al., 2020; Uusitalo et al., 2017). Due to major changes between point source capture and DAC systems it is not possible to copy the findings from the latter studies to this project.
Instead, to still provide a manageable number that allows the studying of hypothetical emissions from the DAC unit in the microplant, the emissions are assumed to fully consist of ammonia. The exact amount of emitted ammonia is assumed to be a function of the lifetime of the sorbent and a sorbent-to-NH3-emission-rate that provides a number for the amount of degradation products that is converted into ammonia. As previously explained, the sorbent is replaced when it is 80% degraded, meaning that on average 20% of the mass of the sorbent forms degradation products.

NH_3 emitted (/ kg CO_2 captured) = 0.2 * Degradation-product-to-NH3 * Sorbent-mass / (avg.-CO_2-production * sorbent lifetime)

All parameters in this equation are tested in the sensitivity analysis to provide a better understanding about the relation between DAC emissions and the environmental profile of methanol produced by the microplant. The obvious secondary adverse effect of sorbent evaporation and degradation is the reduced lifetime of the sorbent in the system, requiring frequent refilling of the sorbent to maintain the CO_2 absorption efficiency. Upstream impacts of sorbent and diluent production then add to the total environmental profile of the microplant. The influence of sorbent lifetime on the environmental profile is also considered in the sensitivity analyses.

4.7. *Microplant embodiment, maintenance, and farm construction*

Polyethylene, steel, and electrical parts for the embodiment of the microplant
The embodiment of the microplant contains the housing (assumed 6kg polyethylene) to shield it from the elements, a printed circuit board and wiring to control all subsystems, and a support system to attach it to the photovoltaic system (assumed 10kg steel). The unit process table of the embodiment can be found in appendix C.

Estimations of the energy and material needs for maintenance
In theory, a badly performing microplant would be marked for maintenance. To keep the performance of the methanol-plant as high as possible, a new or refurbished microplant will immediately replace the decommissioned plant. The decommissioned microplant is then sent to a maintenance facility where, depending on the complexity of the required repair the microplant, it is either repaired locally, sent back to the original manufacturer (OEM), or decommissioned altogether. Because any real-world estimations are lacking, a relatively pessimistic assumption for maintenance is followed, assuming that 1.5% of all microplants need yearly repairs, 1% needs repair at the OEM, and 0.5% is decommissioned. Estimations for the energy and material needs for this maintenance scenario are provided in appendix D..

Storage of methanol and other farm-related infrastructure requirements
Apart from the microplants and the photovoltaic plant, additional infrastructure is required to transport the produced methanol to a central storage unit, and to allow the produced methanol to be transported by road to the nearest port. All other microplant-farm related requirements such as fences, internal paths, and wiring, are included in the LCI of the PV system. It is assumed that approximately 20 kilometres of road are required due to the expected close proximity to the port of Oman, the road has been modelled using up to date LCIs for road construction. The storage of methanol is considered by including a liquid chemical storage tank LCI from the ecoinvent database, scaled to match storage for weekly emptying for a microplant farm of 3250-4000 units. The full LCI is listed in appendix E.

05

Ex-ante LCI

1. Direct Air Capture Unit
2. Alkaline Electrolysis Cell
3. Fluid machinery, Methanol reactor, Distillation
4. Ex-ante LCI of the Photovoltaic system

5. Ex-ante LCI - Future performance of the microplant

As explained in the methodology chapter, semi-structured interviews with experts and in-situ literature analysis of CO_2-based methanol production resulted in a list of potential parameters that could undergo changes as result of general technological developments. From this list a selection was made based on the outcomes of the sensitivity analysis of the first model. Experts were then asked to engage in a discussion on their expectations of certain technological parameters and to motivate their answers by addressing what drivers would cause the advancements in the technology parameters.
Resulting parameters were tabulated in a number of scenarios. The pessimistic scenario consistently describes the system in its current state (lab-scale).

5.1. *Direct Air Capture unit*

Together with the AEC, the DAC unit is responsible for the far majority of the total energy demand. Any energy efficiency improvements of the DAC unit will therefore directly result in better environmental performance.

5.1.1. Optimizing mass transfer in the DAC

Mass transfer (i.e. the CO_2 absorption in the sorbent) can be optimized through better mixing of sorbent cocktails and gradual optimization of the design of the capture column and stripper column. Tangible examples are increases in the total surface area between the sorbent and the air, an increase in the CO_2 throughput to keep the driving force high (into the sorbent), and lower viscosity sorbents to increase diffusion rates. A better mass transfer requires less cycling of the sorbent and also reduces the heating needs, resulting in a lower overall electricity demand. The technology developers expect that through gradual improvements the mass-transfer will be improved significantly.

5.1.2. Heating needs

The 'unloading' of CO_2 and water from the sorbent is an energy intensive process. Currently the observed energy input is twice as high as the theoretical minimum, the tech. developers at ZEF explained that it is likely that the performance will get closer to the maximum achievable efficiency over the next ten years. Partially, energy savings can be realised by optimizing the ratio between the captured water and carbon dioxide. The methanol reactor requires CO_2 and H_2 in a molar ratio of 1:3, preferably the DAC unit therefore needs to produce CO_2 and H_2O in a 1:3 ratio. Any other water mass only results in an additional energy requirement for the vaporization of the water in the stripper column. Potential water recycling after the distillation unit could lower the ratio to around 1:2. In turn this leads to a reduction in the energy requirements at the stripper column as the splitting of water from the mixture requires a lot of thermal energy. In addition, improvements in insulation and the heat exchanger will continue to improve the thermal efficiency of the system, reducing the thermal energy demand and thereby the total electricity demand.

5.1.3. Sorbent degradation

As previously addressed, the degradation of the sorbent depends on the vapour pressure, temperature, surface area, (gas) flow rate, and inter-molecular forces (Gowda, 2020). With an eye on future design iterations the current DAC design has a relatively large absorber, resulting in more surface area. M. Singha explained that the absorber is expected to become smaller which will benefit the lifetime of the sorbent. Current lifetimes under lab-condition are approximately six months. The developers explain that the performance target is a lifetime of four years. However, in a discussion with E. Goetheer the default lifetime of four years was considered rather optimistic (E. Goetheer, personal communication, n.d.).

5.1.4. Parameterization

To maintain a certain level of manageability for the parameters underlying the potential process improvements, all parameters were reduced to global percentual improvements in relation to the LCI compiled in the previous chapter. The technology developers were asked to aggregate their expectations based on pessimistic, neutral, and optimistic assumptions on a short and medium term basis. The result is a table consisting of three core technological parameters and six values per parameter.

Table 9: Ex-ante parameter data for the Direct Air capture system. ST: Short term, MT: Medium term. P/N/O: Pessimistic, Neutral, Optimistic. For an overview of the reasoning behind these parameters, see the goal & Scope definition

Parameter	ST - P	ST - N	ST - O	MT - P	MT - N	MT - O
Electricity demand (kWh/kg CO2)	2.906	2.527	2.148	2.527	2.148	1.895
Sorbent Lifetime (Years)	0.5	4	5	2	4	8
DAC emissions (%NH3/TEPA degradation)	0.5	0.2	0.1	0.5	0.2	0.1

In a reflective session the technology developers agreed that the optimistic short term scenario should be well within reach. Electricity demand reductions of 15% overall were considered realistic and reductions of 25% in the long term optimistic scenario should be possible considering the current position that is still far way from the maximum achievable efficiency.

5.2. *Alkaline Electrolysis cell*

5.2.1. AEC improvements

The performance of the AEC cell can be optimized via multiple routes. For one, the thermodynamics (i.e. temperature, pressure) of the cells can be tweaked to reduce the energy required for the splitting of hydrogen from the oxygen atoms. Another option is to reduce internal energy losses by e.g. minimizing the resistances inside of the cell (Mulder, 2020). Of course, efficiency can also be increased by optimizing the cell and electrode design to make sure that an increased portion of the electricity applied to the cell is used for the production of hydrogen.

The global performance indicators of the alkaline electrolyser are primarily the current density in the stack and the overall efficiency of the application of this current density to the stack. The current density is a function of other parameters whose optimization are mostly a matter of weighing capital and operational expenditures (i.e. OPEX vs CAPEX). In this section these parameters are briefly addressed.

5.2.2. Electrodes

The electrodes for example can be made of bare nickel, which have lower current densities but are cheaper and typically have longer lifetimes. Alternatively the electrodes can be coated (e.g. DLR electrodes) which increases overall current density at the cost of shorter lifetimes and higher production costs. Important AEC parameters such as the current density are therefore related to financial considerations. The future costs of the more advanced electrodes are then highly relevant to the future LCI; The lower the future price the more likely it will become that better electrodes will be used in the AEC, leading to overall better performance.

Global industry learning rates could be applied to estimate the future costs of these improved electrode types. However, the developers at ZEF are relatively confident in their assumption that on the medium to long term the electrodes will have been reduced in price enough to be used in the AEC. This assumption is accepted in this LCA. On the short term it is expected that electrodes will be made of Raney nickel, which causes an average efficiency of 70%. The only exception is the short term pessimistic scenario where electrodes are assumed to be composed of bare nickel with an efficiency of 61%.

The result for the lifetime of the stack is that it is assumed to be around 90.000 hours (or 30 years) by 2030. A similar, slightly higher, lifetime is also considered in the Deloitte technology monitor for hydrogen electrolysers (Perrin et al., 2021).

5.2.3. Current density

In the consultation of the experts the current density was taken as primary ex-ante variable because it was deemed more accurate and appropriate to globally estimate improvements in the current density as opposed to addressing each of its underlying factors and calculating the consequences. This allowed for a more holistic discussion on the potential future states of the AEC sub-system. Assuming a consistent peak power requirement, the result of an increase in current density is a reduction of the amount of cells in the stack, leading to a reduction in the total material requirements for the AEC. The amount of cells were calculated with a spreadsheet provided by ZEF which calculates the peak power per cell based on the current density, the average efficiency and resulting required voltage, and the total area of each cell. The amount of cells is then found by dividing the required peak power by the average peak power per cell.

5.2.4. Parameterization

The results from the semi-structured interviews with the technology developers were aggregated in a few key parameters used in the LCA model. The average electricity requirements are calculated from the expectations about the efficiency of the AEC unit. The total material demand is determined by the amount of cells in the stack, the electrode types, the bipolar plate weight, and the stack lifetime. The use of multiple ex-ante parameters to derive single parameters in the LCA model introduces the problem of 'compounding parameters'. Compounding parameterization occurs when multiple ex-ante need to be stacked to calculate relevant LCI data. An example is the input of nickel; to calculate the total nickel input the stack lifetime and the number of cells are both relevant. Under the short term pessimistic scenario more cells are required and the stack is assumed to be replaced after ten years. This more than doubles the nickel input compared to the next scenario. The compounding parameters of this ex-ante analysis are left unchanged because the purpose of the scenarios is especially to investigate such relations and provide a hypothetical range of impacts that describe the potential future of the microplant.

Table 10: Ex-ante parameter data for the Alkaline Electrolysis system. ST: Short term, MT: Medium term. P/N/O: Pessimistic, Neutral, Optimistic

Parameters	ST - P	ST - B	ST - O	MT - P	MT - B	MT - O
Electricity (kWh / kg H2)	54.645	47.619	47.619	49.020	47.619	44.444
Number of cells in stack	140	121	81	79	49	26
Current density (A/cm2)						
Bipolar plate weight (kg)	3.56E-02	2.13E-02	2.13E-02	3.56E-02	2.13E-02	2.13E-02
Stack lifetime (years and hours)	10 30.000	20 60.000	20 60.000	30 90.000	30 90.000	30 90.000

5.3. *Fluid machinery, Methanol reactor, and Distillation system*

Table 11: Ex-ante parameter data for the compression, methanol synthesis, and distillation subsystem. ST: Short term, MT: Medium term. P/N/O: Pessimistic, Neutral, Optimistic. Large deviations in energy use between scenarios is caused by heat integration (DS) and autothermal synthesis (MS)

FM, MS, DS	ST - p	ST - N	ST - O	MT - p	MT - N	MT - O
FM electricity (kWh/kg of CO_2)	0.58	0.33	0.22	0.33	0.22	0.17
DS electricity / heat use (kWh / kg MEOH)	0.94	0.75	0.69	0.75	0.69	0.14
MS (MJ / Kg methanol)	0.58333	0.5	0.14	0.5	0.14	0.14
MS catalyst lifetime	6	20	20	10	20	25

5.4.

5.5. *Ex-ante LCI of the photovoltaic system*

Estimating future technology parameters of the PV system with the ITRPV roadmap
The global market for photovoltaics has seen major growth and developments in every relevant parameter that make PV adoption more attractive. In short, average costs have drastically decreased, while efficiency has been steadily improving. The cumulative growth of the PV market is expected to cross terawatt-sized milestones in the following ten years (IRENA roadmap, 2019). The global ramp-up of production and research into PV technologies makes it unlikely that the past technological improvements represent the final stages of the respective PV technologies. In this chapter, the most prevalent and relevant expected technological developments for bifacial sing-crystalline panels will be discussed in order to construct an appropriate future Life Cycle Inventory for the microplant system. A number of data repositories will be consulted with a preference for the International Technological Roadmap for Photovoltaics (ITRPV, 2021) will form the backbone for the collection of data. This roadmap was a collaboration between the network organisation VDMA and a collaboration of leading crystalline Silicon (c-Si) producers, wafer suppliers, cell manufacturers, module manufacturers, PV equipment suppliers, production material providers, as well as PV research institutes and consultants. Earlier versions of the ITRPV roadmap have been used in ex-ante LCA studies (e.g. Blanco et al., 2020).

Data estimations are required despite of the ITRPV roadmap
Unfortunately there is a discrepancy between the LCI data as provided by the IEA PVPS task 12 report and the future developments as detailed by the ITRPV report. Many of the material inputs listed in the IEA report are not reflected by the ITRPV report and vice versa. This is likely due to the difference in data collection in both reports. Whereas the IEA views the production chain of single-Si panels mostly as individual black-box processes with only in- and outputs (i.e. on an intermediate product basis), the ITRPV report looks at individual developments on wafer, cell, and module level (i.e. on a process basis). To transform the data from the ITRPV report into useful LCI data, an additional transformation step including subsequent assumptions is necessary.

An additional limitation of the ITRPV data is that no indication is provided about the relation between production process optimization and energy / material inputs per unit of intermediate product. To the knowledge of the author, no global data (as opposed to detailed technology-level data) on future energy efficiency improvements is readily available. This was confirmed in correspondence with technology experts at TNO (M. Späth, personal communication, n.d.). Therefore, the future process optimizations that lead to energy efficiency improvements for the manufacturing of PV panels need to be estimated based on the more detailed process improvement data from the ITRPV report.

5.5.1. Ingot production

In the ingot production (or crystallization) process, solar-grade (Siemens) silicon is melted and crystallized by introducing a seed crystal in the molten mass and inducing crystal growth. The throughput (i.e. speed of production) of the ingot production can be increased by growing more crystals with the same crucible (ITRPV, 2021). The faster ingot growth reduces the heating load per kilogram of silicon ingot and the larger ingot weight per crucible reduces start-up / cycling requirements. The expected increases in both ingot weight is shared in the ITRPV report, approximately 5% by 2025 and 15% by 2031. The crystal pulling rate is expected to increase with an average of 10% in 2025 and 20% in 2031. To match these improvements to the LCI a rough assumption is required. It is assumed that the advancements in throughput result in improvements for 75% of the total energy requirements, the remaining 25% is assumed to be the result of other unknown parameters and remains stagnant. This results in an overall energy demand reduction of 8.6% by 2025 and 14% by 2031. The more efficient use of materials through better internal recycling is expected but not specified by the ITRPV, it is therefore not included in this LCI.

5.5.2. Wafering

In the wafering process the silicon ingots are ground, polished, glued to a glass substrate, and cut with a diamond wire. The thickness of the cut with the diamond wire causes ‘kerf loss’; silicon lost as slurry from the sawing process which is considered a waste in this LCI. The ITRPV report assumes a decrease in kerf loss from 65 to 53 nanometre by 2025 and to 48 nanometre by 2031.
The thickness of the wafers and thereby the amount of material needed for wafer production, is also likely to decrease after a period of stagnation (ITRPV, 2021). For all p-type wafers the approximate reduction in thickness

lies between 9.7% in 2025 and 11.8% by 2031, resulting in wafer thicknesses of 160 and 150 nanometre respectively. For the purpose of this ex-ante LCI, the kerf loss and wafer thickness are combined into a single total width needed per wafer.

As for ingot production, a gradual increase in the speed of the sawing process of approximately 15% by 2025 and 23% by 2031 is reported in the roadmap. Using a similar line of reasoning it is assumed that production speed influences 65% of the energy demand of the wafering process, resulting in approximate energy demand reductions of 7.8% and 11.2% by 2025 and 2031 respectively.

5.5.3. Cell production

Cell production consists of surface texturization, doping, the additional deposition of material layers, the printing of conductive paste on the front and back of the wafer. In short; the cell production consists of pre-treatment of the wafer and application of circuitry. The LCI as retrieved from Frischknecht et al. (2020) contains inputs of metallization pastes for front and back contacts. On the cell level, metallization pastes/inks containing silver and aluminium are the most process-critical and most expensive non-silicon materials used in current cell technologies. The materials in pastes are therefore often a subject of technological improvements. The improvements in metallization paste composition and application for bifacial mono-Si panels can be summarized in the following points:

- Lead in metallization pastes is expected to decrease. The ITRPV only provides the global market shares of lead-free pastes, which are expected to reach 25-35% dominance in 2025 and 65-75% dominance in 2031. These reductions are applied in a 1:1 ratio to the lead content in the metallization paste dataset of the ecoinvent database.
- For bifacial p-type panels the amount of silver per cell is expected to decrease from 95mg to 72mg from 2020 to 2025, and to 57mg in 2031. The reduction of silver per cell is scaled with the respective cell-size.
- Bifacial panels require far less aluminium-type metallization paste and further savings in aluminium use are probable; From about 225mg to 195mg per cell in 2025, and 180mg in 2031.
- The throughput of cell production is expected to increase significantly due to upgraded production lines for PERC structures that have been developed in the last years. All chemical, thermal, and metallization processes will see major developments. As thermal processing throughput is expected to lag behind (i.e. increase the least), this is considered as the main indicator for the overall throughput improvement: approximately 80% in 2025 and 110% in 2031. It is assumed that the improvements in throughput can be applied to 65% of the energy demand for cell production.

5.5.4. Panel production

After cell production is completed the cells are strung together by ribbons or wires in a predetermined architecture that is unique to the panel type. In this case, cells are connected via front-to-back stringing after which they are loaded onto an encapsulant sheet and sandwiched between glass or polymer panels. The edges are then trimmed and sealed with an aluminium frame, and a connector and junction box is added for the electrical installation. The panel is finally cured and tested. The ITRPV report includes material reductions as result of general volume reductions, material substitution and reduction of waste material. Many of the technological advancements in the report cannot be directly applied to the life cycle inventory compiled in this LCA due to the type of reporting being circumstantial. For that reason, only the decreases in solar glass thickness and the general decrease in process energy requirements are taken into consideration. The front-facing solar glass is expected to decrease from 3.2mm in 2021 to 3mm in 2025 and 2.8mm in 2031. Back-side solar glass decreases from 2.8mm in 2021 to 2mm in 2025 and 1.5mm in 2031. Overall process improvements range from 15% from 2021 to 2025 to 20.8% by 2031 assuming that the values reported in the ITRPV report account for 90% of the total energy demand of panel production.

5.5.5. Panel performance

For PERC mono-Si cells the stabilized Cell Efficiency (front-side) of the cell is expected to increase from 22.8% in 2021 to 23.8% in 2025 and 24.5-25% in 2031. However, the cell loses much of its potential efficiency due to shading of module elements, damaging and other adverse effects of its downstream supply chain. The module efficiency is therefore a better indicator. The efficiency for bifacial modules composed of PERC cells will likely increase from 20% in 2020, to 21.6% in 2025 and 22.3% in 2031. The overall module improvements are not directly modelled in the LCI. Instead, it is implemented as percentual improvements relative to the LCI dataset of Frischknecht et al. (2020).

5.5.6. Remaining parameters

For a variety of reasons not all parameters that determine the future performance of the photovoltaic system were taken into account. The missing parameters in this LCI are elaborated in table 14.

Table 12: Parameters that were not considered in the LCI of the photovoltaic plant

Parameter	Comment
Encapsulation thickness reduction (EVA)	Not considered relevant from an LCI perspective
Doping change	From Boron to Gallium, not considered relevant on the scale of this LCA
Thickness of polysilicon for passivated contacts	From 145 nm in 2020 to 80nm in 2025 and 65nm in 2031
Lifetime of coatings	Will double in lifetime by 2031, not included as no proof was found for early decommissioning as result of coating degradation
Cell interconnection types	The share of wires instead of ribbons will increase, resulting in less copper demand. Not included due to a lack of data.
Changes in cell encapsulation materials	Will be partially replaced by Polyolefins (20% in 2031) but not considered relevant by PV supplier.
Cell encapsulation material thickness	Not included due to small differences: 450 to 400 µm from 2021 to 2031
Panel size increase	According to the PV supplier the panel area will remain the same for a considerable time
Cell size increase	Not included due to a lack of data

5.5.7. Parameterization

The retrieved data from the ex-ante research into bifacial mono-Si panels are collected in table 15. All parameters are re-calculated to multiplication factors that are directly applied to the data from Frischknecht et al. A multiplication factor lower than 1 therefore indicates a reduced input of that material or the energy requirements.

Table 13: Ex-ante parameters and their values for the photovoltaic system. Parameters are multiplication factors, meaning that they are used to multiply key unit process exchanges in the initial dataset

Wafer production	2021	2025	2031
Ingot pulling energy improvements	0.925	0.914	0.860
Wafer production			
Kerf loss in micrometres	65	53	48
Cell thickness (half cells)	176	160	150
Total width of ingot needed for cell creation	241	213	198
Total thickness factor	1	0.884	0.822
Wafer production energy improvements	0.971	0.922	0.888
Cell production			
Aluminium (in paste, back side)	0.182	0.158	0.146
Silver (in lead-containing paste, frontside)	0.963	0.730	0.578
Silver (in lead-containing paste, backside)	0.963	0.730	0.578
Lead (in lead-containing paste, frontside)	1	1	0
Lead (in lead-containing paste, backside)	1	1	0
Cell production energy improvements	0.851	0.716	0.634
Module			
Glass Front	3.2	3	2.8
Glass Back	2.8	2	1.5
Glass Front factor	1	0.9375	0.875
Glass Back factor	1	0.714	0.534
Module production energy improvements	1	0.85	0.792

06

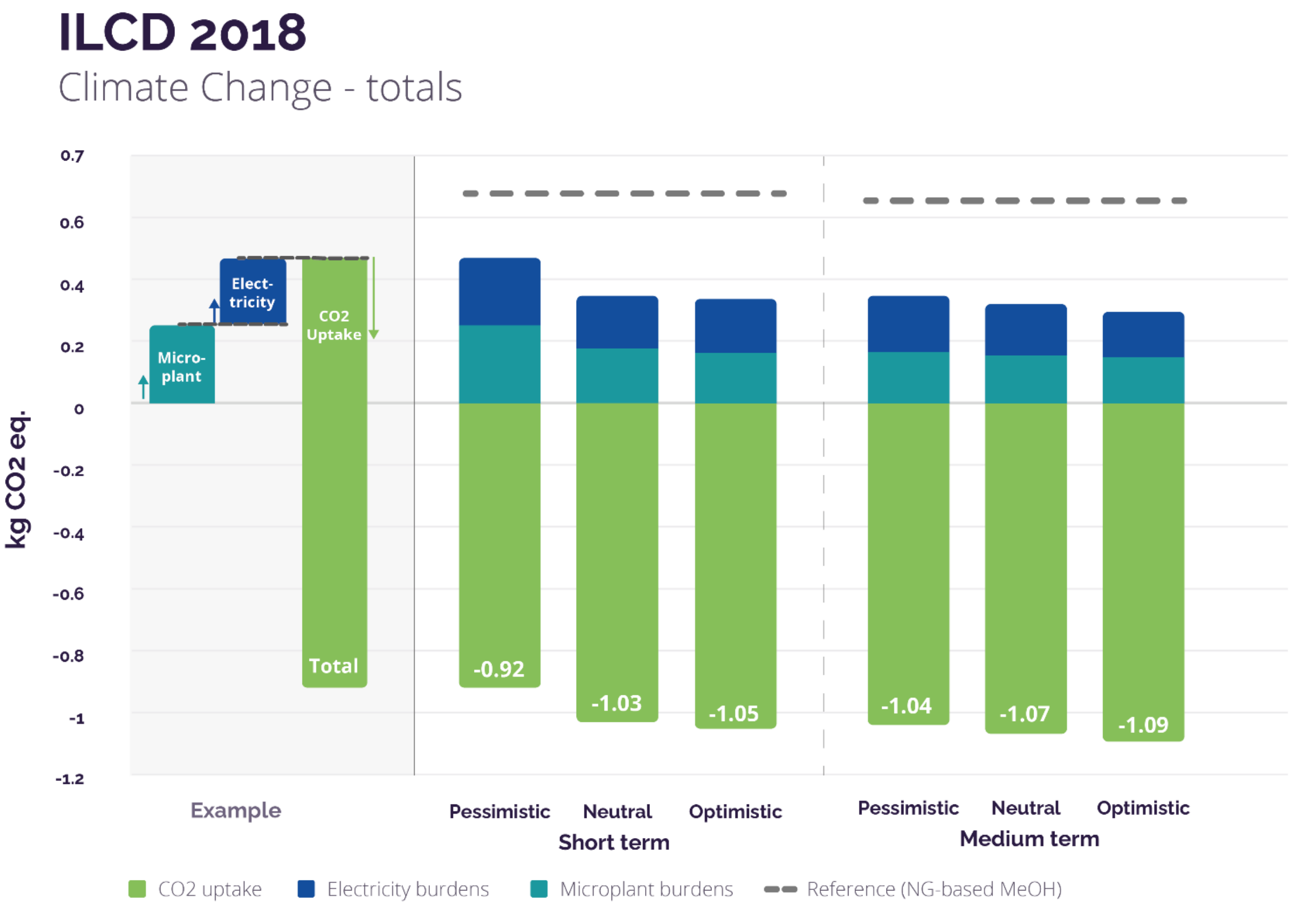
Impact Assessment

1. Lifecycle Impact Assessment: Introduction
2. Climate Change Impacts
3. Ecosystem Quality
4. Human Health
5. Resources

6. Life Cycle Impact Assessment

6.1. *LCIA – introduction*

The life cycle impact assessment is performed using the ILCD 2018 impact method. It divides the impacts in four main categories; Climate Change, Ecosystem Quality, Human Health, and Resources. Individual explanations are provided in the text of the following sections.



ILCD 2018

Climate Change - totals

Figure 10: Climate Change impact scores of methanol from the microplant. The carbon sequestration potential is temporary and is only valid in a cradle-to-gate system boundary analysis. The full life cycle impacts can be derived from this figure by only noting the direct impacts (assuming that 100% of the captured carbon is re-emitted in the end-of-life scenario). The small difference between scenarios is elaborated in the discussion chapter.

6.2. *Climate change impacts*

Figure 10 shows a breakdown of the cradle-to-gate Global Warming Potential of the methanol production by the microplant in farm configuration (n=3250-4000), using photovoltaic electricity and taking into account considerations about the potential future development of the technology. Contributions of the two major systems (i.e. the provision of electricity and the total microplant) are visualised with separate colours.

Though not directly visible from the charts an important finding is that in both the short and medium term scenarios, the microplant impacts are more strongly reduced than the impacts from the photovoltaic system. Due to absence of parameters other than the stoichiometric limit that determine the net-removal of atmospheric CO_2 per unit of output, the total capture of carbon remains stable across all scenarios. The overall decrease in the GWP can therefore be fully attributed to technological improvements in the microplant design, the photovoltaic system, and less significantly also background processes (e.g. manufacturing of raw materials, auxiliary energy).

Taking the short-term pessimistic scenario as example (2025-pessimistic) it can be observed that without the capture of carbon from the atmosphere the impacts would come to 0.47 kg CO_2 eq./kg MeOH. This would still be lower than conventional production of methanol which sits around 0.5-0.8 kg CO_2 eq. /kg MeOH (e.g. Artz et al., 2018; Delikonstantis., 2021). It is advised to consider the impacts visualised in figure 10 without the negative impact scores caused by the temporary sequestering of carbon in methanol due to the inevitable re-emission of carbon dioxide downstream.

No major unexpected differences are observable between scenarios with exception of the short term pessimistic scenario in comparison the other scenarios. The parameters that determine the short term pessimistic scenario are retrieved from estimations based on the technological status of the microplant concept at the time of writing (see chapter 5). This means that most parameters come from early prototype testing and modelling of processes for the prototype design. Other relatively uncertain parameters, such as the electricity requirements for the DAC unit, are based on slightly pessimistic expectations of their performance. The direct result of this exercise is that the GWP impacts are significantly higher compared to neutral and optimistic expectations about the technological performance. The exact contribution of materials and sub-processes will be explained in following sections.
For the pessimistic scenarios, expected improvements in technological performance on the short term and medium term results in a reduction in GWP impacts of -17.2%. For the neutral scenarios, the difference is about 4.5%, a smaller difference due to more similarity between the scenario assumptions. The difference between optimistic scenarios is the smallest; 3.9%, which is due to the expectation that some of the technological parameters will reach their maximum value on the short term, after which significant improvement is not deemed possible with the same microplant design. A tangible example is the efficiency of the AEC unit, which is assumed to reach a maximum (neutral/optimistic) efficiency of 70% on the short term, after which higher efficiencies are not expected to occur on the medium term due to cost considerations.

It can be observed in figure 10 that the max. expected cradle-to-gate GWP of the microplant is -0.921 kg CO_2 eq. / kg MeOH under the *pessimistic short term scenario*. The min. GWP is -1.125 kg CO_2 eq. / kg MeOH under the *optimistic medium term scenario*. The range between these two values as presented in figure 10 is the expected range of the environmental profile of the current microplant concept.

As stated, the overall difference between scenarios is minor. It can be argued that the inherent uncertainty of the ex-ante assessment could introduce a greater variance than is shown in the technology scenarios. This begs the question whether the scenarios indicate significant differences at all. The issue of the technology scenarios vs the overall uncertainty is elaborated in the discussion.

6.3. *Ecosystem quality*

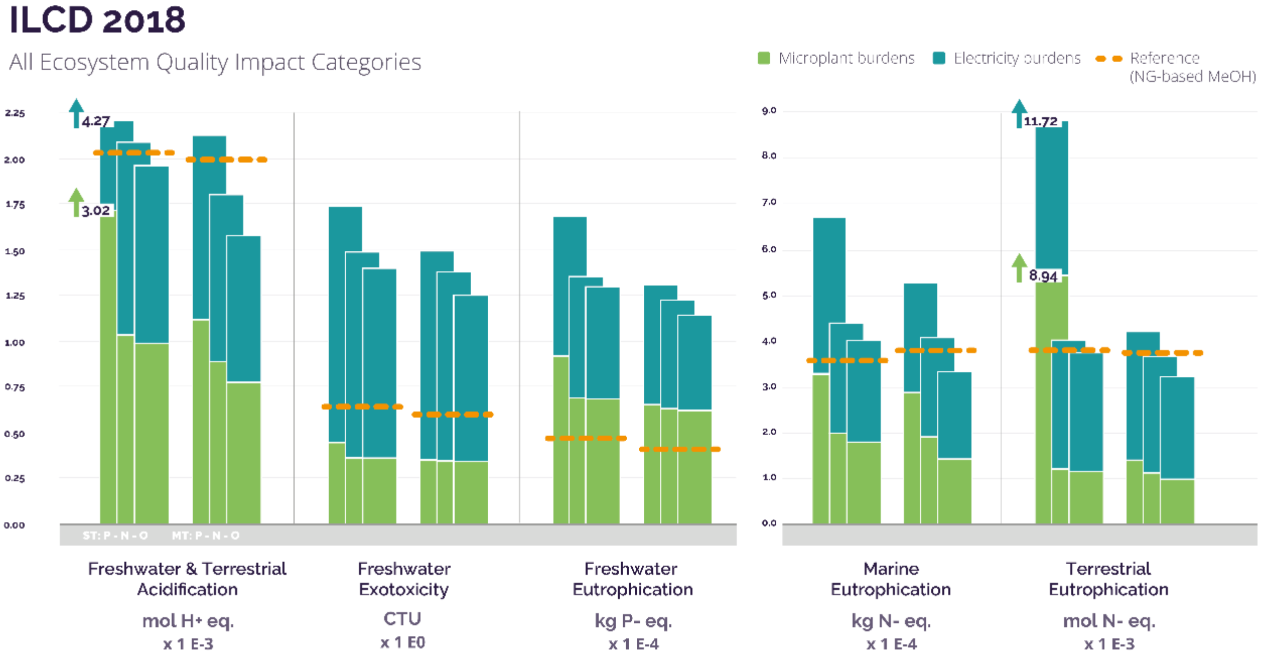


Figure 11: All ecosystem quality impact categories of the ILCD 2.0 2018 impact method. Each category contains the results of all six scenarios. From left to right: Short term - pessimistic/neutral/optimistic, Medium term - pessimistic/neutral/optimistic

The ecosystem quality impact categories (ICs) of the ILCD 2018 impact method aggregate the inventory results in a number of midpoint scores that provide and indication of potential damages to ecosystems. Figure 11 provides an overview of the impact scores of all six scenarios compared to conventionally produced MeOH. In general, it seems likely that the ZEF-methanol will show similar impacts to NG-based methanol in three out of five ecosystem quality categories. In two categories, the microplant shows significantly higher impacts.

The acidification potential (AP), measured in mol H+ eq. / kg MeOH, shows considerable differences between scenarios. The initial outlier is caused by the short term pessimistic scenario, which can mainly be attributed to the increased demand for nickel under the pessimistic design assumption for the stack. The contribution of nickel and other materials will be discussed in following sections. Considering the AP of the conventional production of methanol (0.0021-0.0020 mol H+ eq. / kg MeOH) the microplant performs comparably on the short term and slightly better on the medium term for the neutral and optimistic scenarios. Crucial unpreventable upstream processes for conventional methanol production such as the sweetening of natural gas lead to large direct emissions. The microplant has a clear benefit in that it does not require such detailed conditioning of its feedstocks as it receives pure water and CO_2 from the DAC unit.

As previously introduced, the Freshwater Ecotoxicity (FE) impact category is a measure of the toxic effect of the environmental exchanges of a product system on aquatic freshwater species (Fazio et al., 2018). The impacts in this category are therefore relevant on a local level, which begs some understanding of the contributions behind the results. As it turns out, the means of electricity provision to the microplant is the clear dominating factor in this category. To a large extent (70% of the PV share, 50% of the total) this can be deduced back to the treatment of wastewater from the fabrication of single-Si wafers. Because wafers are produced in a few single locations, it can be reasoned that the impacts are relevant. Other electricity production processes could mitigate these impacts, as will be discussed in later sections.

The microplant shows considerably higher impacts compared to conventional MeOH in the freshwater eutrophication category. Again, the treatment of wastewater from wafer production is a relevant contributing factor (~10% of the total) but major material inputs for the microplant cannot be underestimated. Especially the material requirements for the production of the electronics of the microplant prove to generate high impacts. Copper for the inverter and wiring for example, cause a share of about 18% of the total. Again, most impacts can be traced back upstream to production processes. Understanding these impacts requires knowledge about the impact method and its relation to localized impacts, which should be material for further research if this category is deemed problematic.

For marine eutrophication, the microplant performs slightly worse than conventionally produced MeOH. Direct NH3 emissions of the microplant are a smaller source of the difference with approximately 7% of the total. To better understand the contribution of the DAC unit in this category, a sensitivity analysis is performed in chapter 7. Another DAC-based contributing factor is the production of the sorbent, which under the default assumptions is responsible for about 14.5% of the total impacts due to impactful primary feed chemicals. Under the ST-N scenario, the shorter lifespan (see next paragraph) causes an additional need for sorbent manufacturing and thus a higher marine eutrophication score. The choice of sorbent therefore seems to be relatively important in this category.

The same factors are relevant in the Terrestrial Eutrophication category, in which the microplant performs comparably to the reference system with exception of the first short term pessimistic scenario. The direct emissions of the DAC unit lie somewhere between 19% and 59% of the total emissions depending on assumptions about the degradation rate of the sorbent and its relation to resulting emissions. The large outlier of the ST-N scenario is therefore almost entirely the result of a pessimistic assumption about the sorbent degradation and related direct emissions. To restate this pessimistic assumption: in the ST-N scenario the sorbent has a lifetime (i.e. until the sorbent is degraded for 20% of its total mass) of 1 year, or 2900-3000 operational hours, it is then assumed that 50% of the degraded compounds is turned into NH3 emissions. High impacts in this category that are a result of direct emissions could be an indication of potential damage to local (sensitive) ecosystems. The relation between emissions and inflicted damage is bound to local conditions and depending on the local context can be relevant or not.

It should also be noted that, considering the likely desert-based future location of the microplant farm, the eutrophication potential would not be as significant as it would be for lush and urban environments. One often mentioned critique of LCA is its inability to appropriately model impacts on a local basis. This topic will be continued in the discussion.

6.4. *Human Health Impact categories*

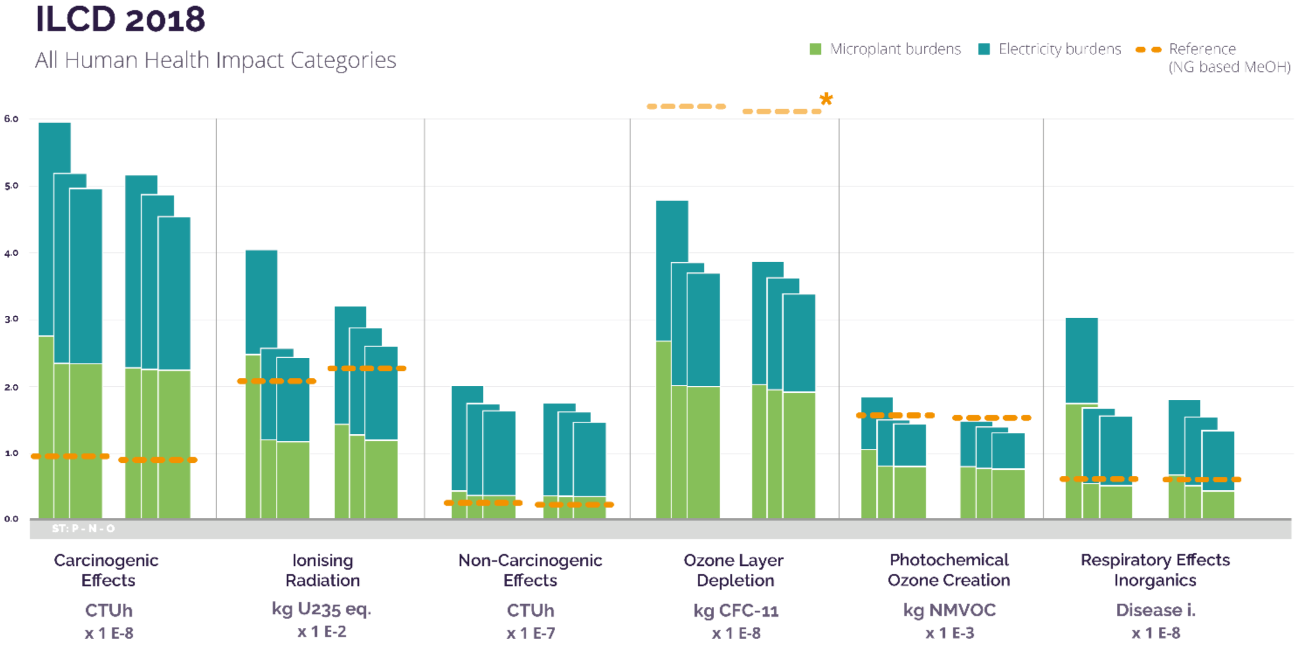


Figure 12: All ecosystem quality impact categories of the ILCD 2.0 2018 impact method. Each category contains the results of all six scenarios. From left to right: Short term - pessimistic/neutral/optimistic, Medium term - pessimistic/neutral/optimistic. *: *Falls outside of the range of the chart (2.19E-7 and 2.18E-7 respectively)*

The ILCD 2018 impact method includes a subcategory for the impact categories that can have adverse effects for human health. Figure 12 shows the impact scores from the LCA model for both methanol produced by the microplant in its six scenarios and the reference NG-based MeOH production. Contrary to the Ecosystem Quality ICs, differences in orders of magnitude can be observed. Overall, the relative contribution of electricity production and all other microplant-related impacts are rather equal, the only exception being the non-carcinogenic effects IC where the burdens of the upstream PV processes dominate the total score.

In the carcinogenic-effects category, the microplant showcases impacts that are a fivefold higher than NG-based MeOH. For a large part, the difference can be explained by the difference in total material requirements between both forms of methanol production. The production of materials, and especially metals, generally receive high impacts for the carcinogenic effects impact category. The steel and aluminium requirements for the mounting system of the photovoltaic panels and the steel required for all parts of the microplant contribute significantly with about 17% and 34% respectively of the total impacts. Similar to the ecosystem quality – ecotoxicity IC, the treatment of wastewater from the panel production appears relevant as well, representing approximately 20% of the total impacts. In the non-carcinogenic IC the same difference can be identified, albeit a slightly larger difference (about 6-8 fold). The production of raw materials is not as relevant as in the carcinogenic effects IC and most of the impacts can be deduced back to the wafer wastewater treatment and the production of electronics for the microplant (approx. 12%).

In the Ionising Radiation IC the two means of methanol production perform comparably. This particular IC will not be as relevant as the others, as it tries to capture all up- and downstream emissions that cause ionising radiation. Ionising radiation can be relevant for some cases and can be problematic due to its potential to interact with and change molecules or cells. In this case however, there are no sources of ionising radiation that can be significant. The only apparent interesting feature is that the production of the sorbent is relevant in this category, explaining the initial higher value in the ST-N scenario due to the assumed shorter sorbent lifetime. ZEF-methanol clearly has a lower ozone layer depletion potential than NG-based methanol. In this particular IC, NG-based MeOH scores ten times higher than the microplant due to major upstream emission sources coupled to gas production and transport. For the ZEF-methanol, over half the impact score is the result of emissions from the production of polyethylene terephthalate (PET). PET is used both in the encapsulation of solar panels

(29% of total PET) and for the production of polyester fibre that is used in the air filters of the DAC unit (71% of total PET). These filters need to be replaced occasionally and their lifetime therefore has a significant impact on this impact category. However, the use of polyester fibre in the air filters is partially an assumption, and other materials can be used as well.

The photochemical ozone creation category addresses emissions of nitrogen oxides (NOx) and non-methane volatile organic compounds (NMVOC's) and their potential to form ozone. The presence of ozone can damage vegetation and be harmful to human respiratory tracts. Direct emissions from the microplant can be significant in this IC (28% of the total). The methanol synthesis sub-system purges a part of its contents to reduce the accumulation of nitrogen and to measure its contents. Methanol is expelled from the system via the purge and causes the formation of ozone according to the ILCD 2018 impact method. These direct emissions are not enough to cause any significant difference with NG-based MeOH but it could become a local site-based problem.

In the respiratory effects – inorganics IC the microplant causes a number of upstream and direct impacts that lead to a rather high score in comparison with NG-based MeOH. The photovoltaic system generates most of the impacts which can be further traced back to the larger solar glass requirements of the bifacial panels (22%) and the construction of the plant (5%). Direct emissions from the DAC add 8% to the total impacts caused by the degradation of the sorbent into ammonia. Ammonia emissions can play a large role in the formation of fine particulate matter ($PM_{2.5}$) which in turn can impact human health (Schifer et al., 2014). Upstream impact sources as the bifacial panel production do not fall within the sphere of influence of ZEF, the direct emissions however, can be a potential source of impact mitigation.

Overall the microplant seems to perform worse in four out of six impact categories that are relevant for human health. In none of these cases do the scenarios have much effect on the overall comparison. In three ICs, the impacts of the microplant alone (i.e. without PV electricity) lead to higher impacts compared to conventional methanol production, the usage of other types of renewable electricity would therefore not be able to turn the tide in favour of the microplant.

6.5. *Resources*

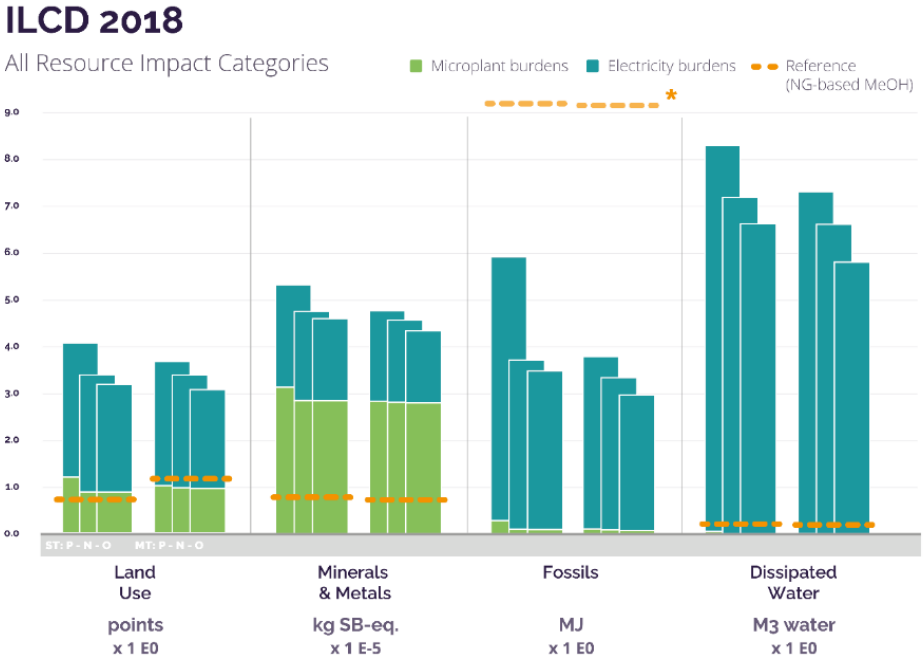


Figure 13: Impact results in the ILCD 2018 resources categories

The ILCD impact method considers resource use in four distinct impact categories. Not all impact categories are as relevant to this research or provide as many insights as others. Land use for example is an obvious loss for the microplant due to the large surface area required for the solar panels. Dissipated water can also fully be attributed to the photovoltaic system, more specifically to the production of silicon which requires vast amounts of water. The production of clean and pure water by the microplant is not considered as mitigating factor in this category due to the absence of plans to catch and transport water to appropriate destinations. Yet, if this would be taken not consideration it would still not counteract much of the total dissipated water impacts as only 0.57l of water is produced for every kilogram of methanol. Regardless, on a more practical level the usage of water in areas where water is plentiful (i.e. industrial countries) and the production of water in areas where water is scarce (i.e. desert locations for the microplant farm) can be reason enough to debate whether the representation of these impacts are realistic.

The minerals and metals category is more interesting as it provides a measure of the total material demand by both ZEF-methanol and conventionally produced methanol in a time where renewable energy technologies compete for resources. The microplant itself contains some inputs that cause high impacts in this category. The production of the catalyst in the MS reactor for example stands for over 16% of the total impacts due to its zinc-oxide and copper contents. The production of wiring and PCBs for the macroplant's control systems and the inverter of the AEC is responsible for another 41%. For the photovoltaic system the production of metallization paste, used in the application of conducting layers on the wafers, is the primary contributing factor together with the production of solar glass (15% and 11% respectively). Natural-gas based methanol on the other hand shows low impacts in this category, largely due to the centralized production at facilities with high production rates, thereby reducing the overall material requirements per unit of output.

Naturally conventional production of methanol requires vast amounts of fossil feedstocks, leading to an overall fossil demand of 32 MJ for both heating and chemical feedstocks. The microplant scores a tenfold lower compared to its conventional counterpart and remaining impacts can mostly be traced back to the still heavily fossil Chinese energy mix where most of the parts are produced.

The resources impact category does not produce results that are really striking. Still, the higher input requirements for minerals & metals could be an important factor of comparison with alternatives if resource use becomes more important in the following years as the result of global competition for materials.

07 | Interpretation |

1. Consistency and completeness check
2. Contribution analysis
3. The role of electricity
4. The material demand of microplant-based methanol
5. Other sensitivity analyses

7. Interpretation

The general overview of the impacts gives an initial outlook on the environmental performance and profile of methanol produced via the microplant concept. What normal impact assessment fails to add, is a further understanding on the composition of the environmental profile, and more importantly, what the role of methodological/technological assumption are on the impact results. Under the ISO guidelines, LCA studies should therefore include a section that attempts to provide more depth and understanding; the interpretation phase. This chapter elaborates on some of the mandatory components of the interpretation phase and includes contribution and sensitivity analyses. Sensitivity analyses in this study are performed on a practical level, meaning that instead of calculating a sheet of important parameters that are difficult to communicate, a set of logical alternatives and variations are explored.

7.1. *Consistency and completeness check*

7.1.1. Consistency check

Guinée et al. (2002) developed a checklist to assess whether data choices have been made consistently over the product's life cycle or across options. It includes 1) Difference in data sources (regarding the hierarchy of unit process data), 2) Differences in data accuracy, 3) Differences in technical (maturity) level, 4) temporal differences, 5) differences in data age, 6) differences in geographical representativeness, and 7) differences in the functions performed by the alternatives.

Many of these topics have been addressed in this study already, mainly in the LCI chapter. The more methodologically relevant topics are discussed in the discussion chapter. Besides the large differences in technical maturity level, and the data age of the microplant in comparison with conventional methanol, no serious consistency problems were observed. This does not mean that all insights in these chapters can be copied blindly, please refer to the discussion about the validity of the results.

7.1.2. Completeness check

Guinée and colleagues furthermore advise to subject the performed LCA to the critical eye of LCA experts to validate whether the correct flow diagram was modelled, whether all processes were included, whether economic or environmental flows could be missing, and to check total emissions and mass balances. Within this study, these checks are performed by comparing the results to and procedure with those in comparable literature. This entire exercise received its own chapter. All other checks will be performed by the supervisors.

7.2. *Contribution analysis*

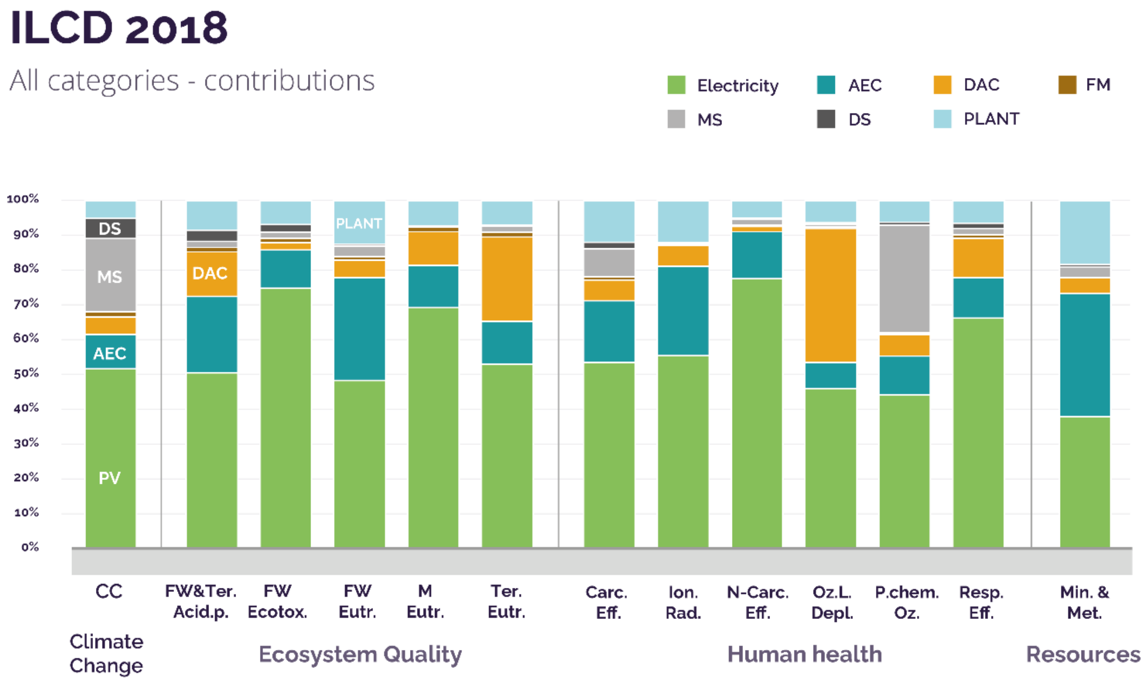


Figure 14: Contributions on sub-system level, using the medium term – neutral scenario. DAC: Direct Air Capture unit, AEC: Alkaline Electrolysis Cell, FM: Fluid mechanics (CO2 compression), MS: Methanol Synthesis reactor, DS: Distillation unit. Plant: All embodiment (both microplant embodiment, maintenance, and farm infrastructure).

A contribution analysis of the short term neutral scenario

To better direct research efforts into the areas that are most relevant, a contribution analysis is performed to gauge where most impacts reside per category. Figure 14 provides the overview of the analysis, which was performed using the Sankey analysis tool in the Activity Browser and manually calculating resulting shares. Figure 14 shows the relative contributions at sub-system level, meaning that all flows are aggregated on the level of individual subsystems within the microplant. The photovoltaic system is aggregated as well, resulting impacts are not allocated to individual processes. The PLANT share stands for all impacts resulting from the embodiment of the microplant (e.g. wiring, electronics), the maintenance of all microplants (e.g. repair, replacement), and all infrastructure required for the microplant farm (e.g. methanol storage, pipelines, roads). The contribution analysis was initially performed under all scenarios. Yet, with a few exceptions, the difference between the major contributors between scenarios was small and not all charts are therefore shown in this section. Figure 14 provides the overview for the medium term neutral scenario.

The relevance of direct emissions from the methanol reactor

In the Climate Change category, there clearly is an increased contribution that originates from the methanol synthesis reactor. As previously addressed, the MS system purges a part of its contents to rid the reactor of accumulated nitrogen and to measure its contents. The purged gasses then cause a variety of impacts. Still, in the climate change category the purged gasses are not very crucial, as the carbon dioxide that is expelled from the reactor has been captured moments ago by the DAC unit. The trace amounts of methanol in the purge gasses that are vented to the surrounding air are relevant however, due to the potential of methanol vapor to form ozone, leading to a higher photochemical ozone creation score (Andersson-Sköld, Grennfelt & Pleijel, 1992). Consequently, apart from the upstream photovoltaic impacts, the methanol synthesis reactor is the primary contributor in the photochemical ozone creation impact category.

The material demand of the AEC leads to major impacts across all categories, but data might overestimate impacts

The alkaline electrolysis cell is responsible for the majority of the microplant impacts in 8 out of the 13 impact categories. The large nickel demand for the production of nickel cells in the stack leads to high impacts in specifically the freshwater eutrophication and mineral and metal resource use categories. The amount of nickel for the production of the cells is in part determined by the electrode type that under the default assumptions is assumed to be bare(pure)-nickel. The effluent of nickel electrode production is furthermore highly carcinogenic but because electrode production is not a process in the database, this is not included in the assessment. The stack, i.e. all cells of the AEC, plays a steady role in all remaining impact categories, on average accounting for between 3-8% of the total impacts in each category. The lifetime of the stack is therefore very relevant and in part explains the difference between the short term pessimistic scenario and the other scenarios that can be seen in the impact assessment. In this scenario, the stack lifetime is assumed to be ten years, therefore demanding replacement halfway the lifetime of the microplant, doubling the adverse effects of the stack per kg of produced methanol over the microplants' entire lifecycle.

Besides nickel contents the material-based impacts of the AEC can largely be traced back to the 2.5 kW inverter for the AEC subsystem (16% of microplant-related impacts in the CC IC). This inverter is in fact a proxy for the actuator for the stack that still has to be designed, due to expected similarities between the inverter and the actuator this proxy was deemed suitable. Most of the impacts of the converter then originate from both the copper input (17.8% of 16%), and the required integrated circuits (i.e. chips)(17.3% of 16%). Other large contributors to the inverter impacts are the printed circuit boards and the other electrical components (26.5% of 16%). A quick review of the background data reveals that the heat and electricity requirements for the integrated circuits are high and that the data can be dated back to 2007 (Lehmann et al., 2007). It can be reasonably expected that the energy requirements for the production of chips has reduced drastically since 2007 due to global process improvements. The total impacts related to the inverter will therefore likely be lower than calculated in this contribution analysis. Regardless, in other impact categories such Freshwater eutrophication, the electronics for the AEC lead to a combined 28% of the total impacts in that category. Other eutrophication categories suffer less from the impacts of the electronics, ranging from about 6-12% of the total impacts. The last category where the AEC electronics are significant is the non-carcinogenic effects IC where the electronics account for roughly 10% of the impacts.

Direct emissions of the DAC unit relevant in eutrophication and acidification categories

In four of the thirteen categories the direct air capture unit matches or surpasses the AEC in its total contribution. Two key contributing factors can be identified. For one, the DAC unit also exhibits direct emissions in the form of ammonia as degradation product from the sorbent. The result is relatively large impacts in all eutrophication categories and depending on the specific sorbent degradation rate can form the most relevant overall contributing factor. The second contributing factor is the DAC's demand for consumable products, for example the sorbent, the diluent and the air filters. In the impact assessment overview it could be seen that the microplant has a relatively high score in the ozone depletion category, this can be almost fully attributed to the air-filters of the DAC unit that under current assumptions need to be replaced every four years to keep filth from entering the system.

The most notable consumable of the DAC is of course the production of the sorbent and diluent (10% of the total microplant GWP impacts, assuming a default lifetime of 4 years for the sorbent at 8 operational hours per day). It is important to note that again, this value is highly dependent on multiple assumptions and modelling choices such as the lifetime, production impacts, and method of allocation. Some mitigating factors for sorbent impact can be found in the modelled sorbent production process, which at the moment is relatively inefficient and might underestimate the efficiency of current industrial sorbent production. On the other hand the default assumption of the sorbent lifetime could be relatively optimistic (E. Goetheer, personal communication, n.d.), counteracting part of these mitigating factors. However, because sorbent production is not relevant to the other impact categories, it can deducted that the sorbent relative to all other technological parameters is not of crucial importance.

CO_2 compression and methanol distillation not relevant compared to other systems

The remaining two microplant subsystems, the CO_2 compression system and the distillation system nearly disappear in the contribution graph. Direct emissions as result of distillation make the DS subsystem visible only in the climate change category. The impacts of these two systems in all other impact categories can only be attributed to the production of steel for their parts. The compression system (FM) is currently assumed to make use of very inefficient standard fridge compressors and therefore will see significant improvements on a sub-system level. Still, in the contribution overview any efficiency improvements in material use will not be very significant.

Other requirements for the farm are not very relevant
The PLANT contributions, indicated by light blue in figure 14, prove to be somewhat of a surprise for the overall impacts. As explained, PLANT stands for an aggregation of maintenance, microplant embodiment, and microplant-farm infrastructure. The latter appears to be irrelevant as the total energy and material requirements for the construction of external and internal roads, small pieces of pipeline, and storage tanks for methanol nearly disappear in comparison with the material requirements for the microplants and the photovoltaic system.

The embodiment share consists of a housing for the DAC unit made of polyethylene, a section of pipes for the transport of methanol from the microplant to a central pipeline, printed circuit boards and ribbon cables/normal wiring for the connection of internal electric components. On average, these electrical components account for between 2-5% of the total impacts across all categories. Again, the use of printed circuit boards and logic circuits are coupled to high impacts. Additionally, the production of copper for all wiring needs further add to the mentioned 2-5% impacts.

Maintenance, due to the relation to the total material demand, is relevant across categories
Maintenance accounts for 11% of the microplant-related impacts in the Climate Change category. Yearly maintenance requirements estimates are currently relatively high, with respectively 1.5% of the microplants that need to be repaired, 1% of the microplants that need to be refurbished at the original manufacturer, and 0.5% that is decommissioned and replaced. The complete maintenance scenario for the microplant adds a significant weight to the material demand over the entire lifecycle of the microplant and is thus relatively evenly spread out across all impact categories.

The decommissioning of the microplant, includes material separation and consequent appropriate treatment of material flows. Due to the cut-off approach, most of the material recovery is not included within the system boundaries. Only the treatment and incineration of plastics that are unlikely to be recovered are attributed to the microplant, these form the majority of the microplant-related impacts in the ecotoxicity and carcinogenic effects categories.

Table 14 places the maintenance impacts in perspective with other major lifecycle stages.

Lifecycle phase	Climate change Contribution
Manufacturing	59%
Transport (microplant)	2%
Operation (consumables)	22%
Maintenance (new material input)	11%
End-of-Life	6%

Table 14: Contributions of life cycle stages to the climate change category.

The manufacturing phase of the microplant in China contributes most to the GWP impacts that are unique to the microplant in its farm configuration with 59% of the total GWP impacts. The combined impact of the consumables is 22% and includes KOH for the AEC, the diluent, sorbent, and air filters for the DAC unit. Impacts related to transport (1-2%) are taken separately from the other phases although they inherently are part of every phase. Transport by sea for sorbent replenishment and initial microplant transport is the main contributor for impacts related to transport.

7.3. *The role of electricity*

The production of electricity to fulfil the energy demand of all microplant-processes is the single most impactful *external* contributor in most impact categories. Any changes in the impacts of the electricity-generating system therefore would be of major influence to the total environmental profile of methanol produced via the microplant concept. This section explorers the role of electricity for the microplant. The first part consists of analysing contributions within the modelled PV system to better understand the impacts and to assess whether or not the calculated impacts seem correct. A sensitivity analysis is also performed on the carbon intensity of the PV system, exploring the correlation between the carbon intensity of the electricity supply, and the CC impacts of the microplant. Lastly, a brief discussion explores potential other modular renewable energy technologies that could be potential contenders.

7.3.1. Contributions

Clearly the impacts of the microplant are closely intertwined with the impacts of the electricity generating system. In this section, the contributions of the major upstream processes of the photovoltaic system are briefly visited to better understand the composition of the microplant impacts and to provide a foundation for the scouting of alternative renewable energy technologies that might mitigate some of the more relevant impacts.

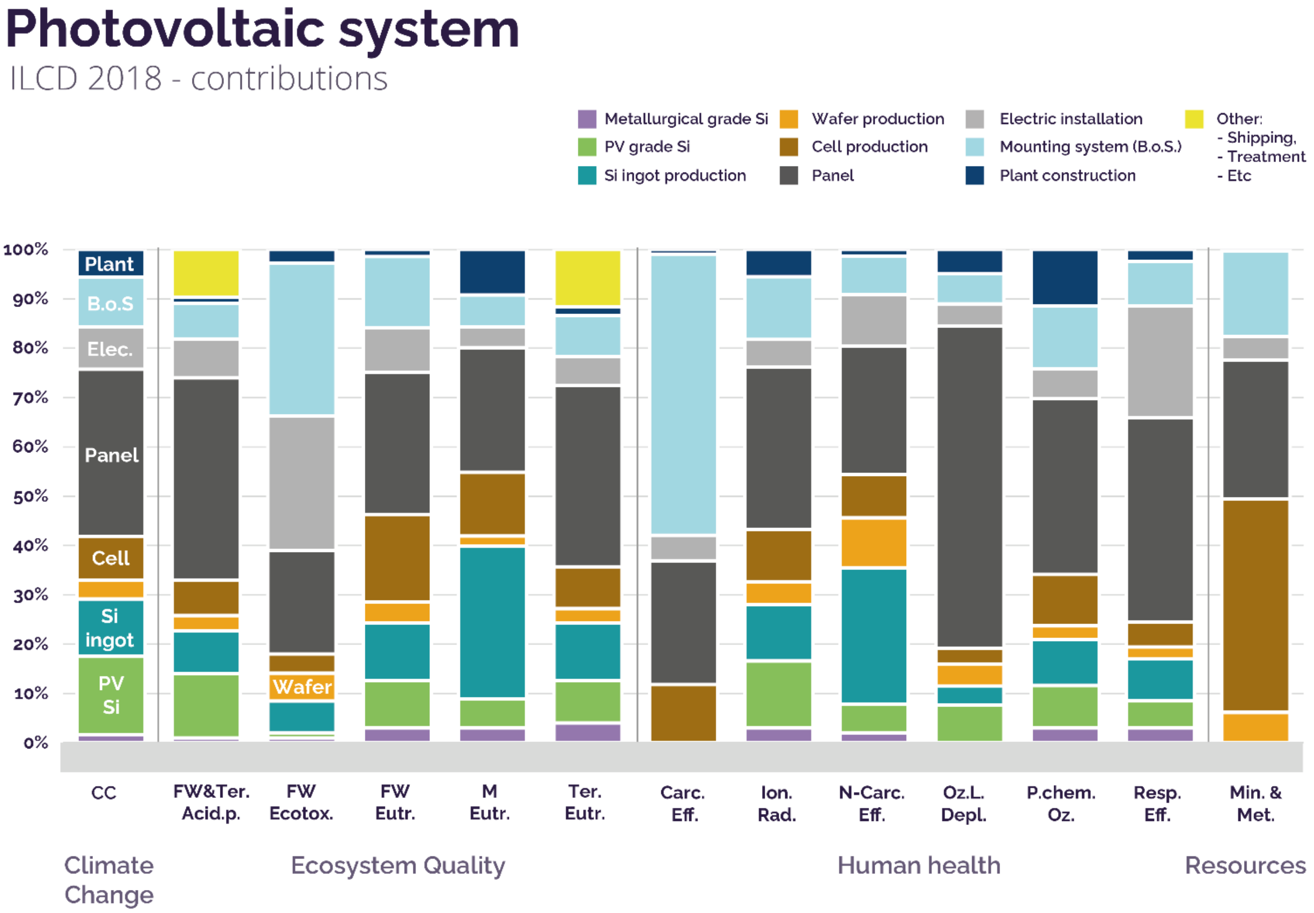


Figure 15: Contributions of individual processes to the overall impacts of the photovoltaic system

Panel production relevant due to solar glass, aluminium, and plastics

A clear contributing factor is the panel production process, which consist of the cutting of the cells, their front-to-back stringing, the loading of the cells onto glass sheets, and the application of the panel frame and connection/junction box. In this LCA, the production of solar glass for the double-glass enclosure of the cells leads to large impacts in the Climate Change, acidification IC, ozone layer depletion, and the respiratory effects categories. The production of solar glass is still relevant but not as prominent in all other impact categories. The aluminium input for the frame is relatively even in all categories with an average contribution of 5-7%. Other material inputs for the panel production such as glass fibre reinforced plastic, PET, and polymer foil and films, contribute a combined average of 4-5% in each category. An exception is the Ozone Layer Depletion IC where the production of PET dominates the other impacts with 32%. The dominance of panel production in the overall PV chain is questionable and generally not found in recent LCA studies on solar panels (e.g. Müller et al., 2021). In this study most of the dominance can be attributed to the production of solar glass which is required for both the front and the back of the panel. Yet, the average amount of glass input for a single side is in line with recent literature (e.g. Frischknecht et al., 2020; Méndez et al., 2021). The difference is therefore likely the result of an out-of-date inventory for solar glass, or the methodological choices in other papers, such as avoided burdens for E.o.L. glass recovery.

High energy demand for silicon production and upgrading in line with literature results
The high energy demand for both the production of solar-grade silicon and the smelting/production of ingots make these two processes relevant in most impact categories, especially because the Chinese energy mix is still impactful in most categories in the used background scenario (from Mendoza-Beltran et al., 2018). The processing of affluent from the PV-grade, ingot production, and wafer production processes is important in the eutrophication categories and the non-carcinogenic effect category.
The large contributions of the mounting system in both the ecotoxicity and carcinogenic effect categories can almost entirely be traced back to the high demand for steel. Other material-related impacts in the ecotoxicity IC is related to the production of wiring for the electric installation. The treatment of waste-plastic from the electric installation at the end-of-life is furthermore one of the main contributors to the respiratory effects category.

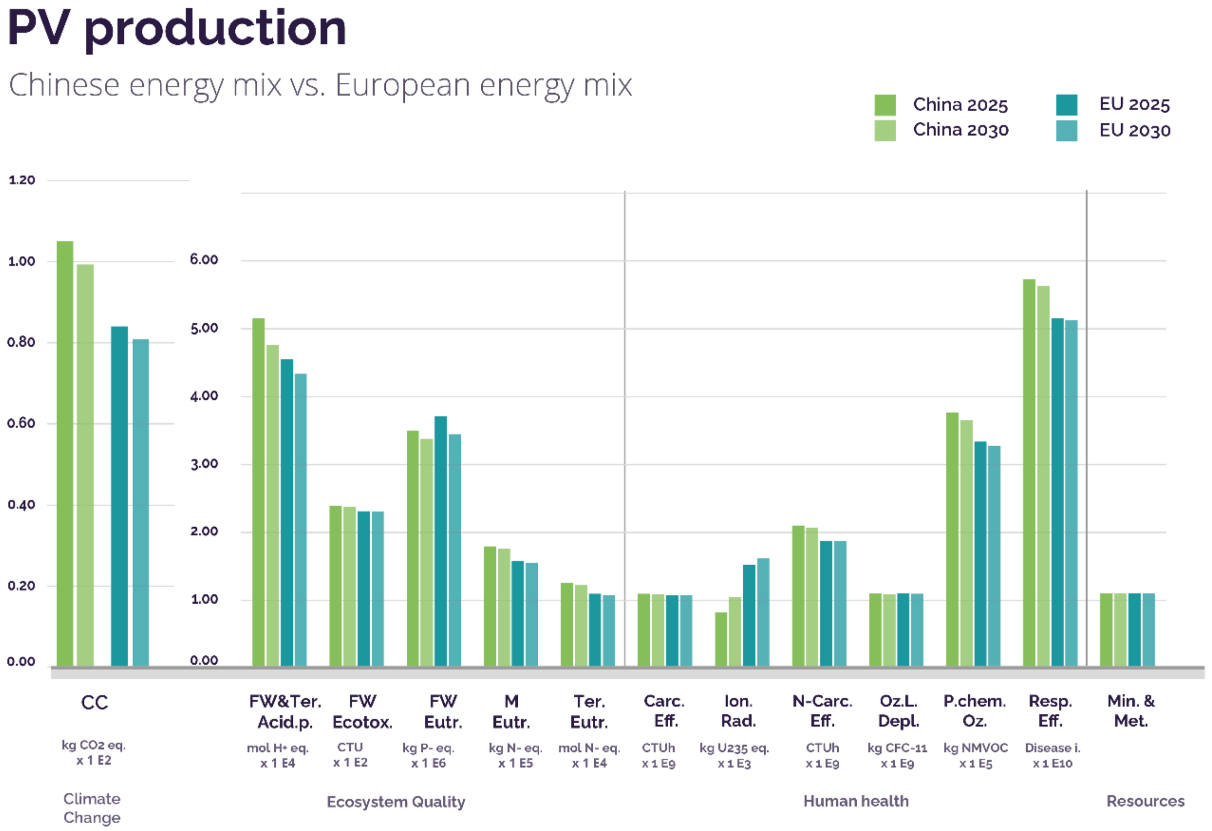
Overall, the role of the panel production process, the electric installation, and the mounting system, seem counterintuitive. Consequently, these processes also show the greatest variation between LCA studies on PV technologies. Large efficiency improvements that have been recently introduced, by for example opting for frameless panels, are possible to mitigate the total impact.

These contributions are not applicable beyond this study
A unique feature of the microplant is its integration with photovoltaic panels. This means that the inverter that is typically a part of the LCI of the PV system is not included in the PV LCI. Instead, the microplant contains an electrical unit that roughly has the same function as a dedicated and integral part of its design. The overall material demand of the PV LCI in this study is therefore lower than an average normal PV plant.

7.3.2. Production location of PV panels

Electricity mix is a crucial background factor for the overall impact of the PV system
The electricity mix alone, accounts for 41% of all impacts in the CC category for the photovoltaic system. China is relatively poor in cleaner energy-carrying resources such as natural gas but is rich in coal. Therefore, the Chinese energy mix still largely relies on coal for its energy needs. Following the background scenario of this study (i.e. from Mendoza-Beltran et al., 2018) we can see that the carbon intensity and most other impacts of the Chinese energy mix decline. However, the use of coal is not entirely phased out and remains an important part of the energy mix under the SSP2.6 scenario.

Production in Europe is a potential mitigation strategy
With the growth of the European PV market (Frauhenhofer ISE, 2020), it becomes increasingly attractive to purchase PV panels from European manufacturers. To assess the potential influence of moving manufacturing to Europe, the Chinese energy mix is replaced by the average European energy mix (without Switzerland) in the PV LCA model. The actual change of location would also involve more efficient energy use (Frischknecht et al., 2020) but that is not included in this analysis.
Figure 16 shows the impacts of moving manufacturing from China to Europe. It can clearly be seen that this results in a significant improvement in most impact categories. Only freshwater eutrophication and ionising radiation show higher impacts, the latter can be traced back to the higher incidence of nuclear reactors in the EU. The influence of the background scenario is larger for China-based production. This is likely the result of the consistent phasing out of coal in the energy mix and replacement by renewables. In neither of the impact categories however, is this enough to outperform production in the EU.
The initial CC impact reduction of about 20% in 2025 and 18% in 2030, would similarly result in significant improvements in the CC impacts of the microplant.



PV production

Chinese energy mix vs. European energy mix

Figure 16: Influence of the European energy mix on the impacts from PV electricity. Functional unit: 1 kWh of PV electricity.

7.3.3. PV scenarios and their impacts

The exact role of the future technological developments of the photovoltaic system in the scenarios of the microplant is challenging to ascertain from the impact assessment figures alone. Table 15 therefore lists the changes in the PV impacts relative to the year 2021.

On average, and without including the outlying ionising radiation scores, the impacts decline with 7% between 2021 and 2025 with a standard deviation of 3%. For the period between 2021 and 2030 the decline is 13% with a standard deviation of 5%.

As can be expected, all categories decline with a certain minimum due to the compounded effect of both foreground technological parameters, and energy-mix-related changes in the background scenarios. The latter also explains why ionising radiation impacts increase (i.e. global increase of nuclear energy). The largest increases can be found in categories where the energy mix is most important (e.g. climate change) and smaller differences are found in categories that are typically associated with impacts related to background material use (e.g. carcinogenic effects).

Table 15: The influence of the PV scenarios on the impacts of electricity compared to the 2021 scenario.

Method	2021	2025	2030
CC - Climate Change total	100%	93%	83%
EQ - F.W. &Ter. acidification	100%	92%	80%
EQ - Freshwater ecotoxicity	100%	98%	95%
EQ - Freshwater eutrophication	100%	93%	86%
EQ - Marine eutrophication	100%	92%	86%
EQ - Terrestrial eutrophication	100%	92%	85%
HH - Carcinogenic effects	100%	98%	97%
HH - Ionising radiation	100%	91%	110%
HH - Non-carcinogenic effects	100%	94%	89%
HH - Ozone layer depletion	100%	96%	93%
HH - Photochemical ozone creation	100%	93%	86%
HH - Respiratory effects, inorganics	100%	94%	88%
resources, minerals and metals	100%	87%	79%

7.3.4. Sensitivity of the microplant to the CC impact of the electricity

To investigate the relationship between the carbon intensity of the electricity supplied to the microplant and the climate change impacts of the microplant, a sensitivity analysis was performed using five minimal and extreme data points. The result is a graph that describes the linear correlation between the carbon intensity of the electricity supply and the total climate change impact scores of the microplant. The graph can be used to (quite roughly) estimate the CC impacts of the microplant if other types of electricity production with other carbon intensities are used.

To put things into perspective, the carbon intensities of on- and offshore wind from the ecoinvent 3.7.1. database are included in the figure. Other photovoltaic technologies such as cadmium-telluride and perovskites-based (tandem) solar cells, were not included due to their relatively outdated datasets in the ecoinvent database and resulting high impacts.

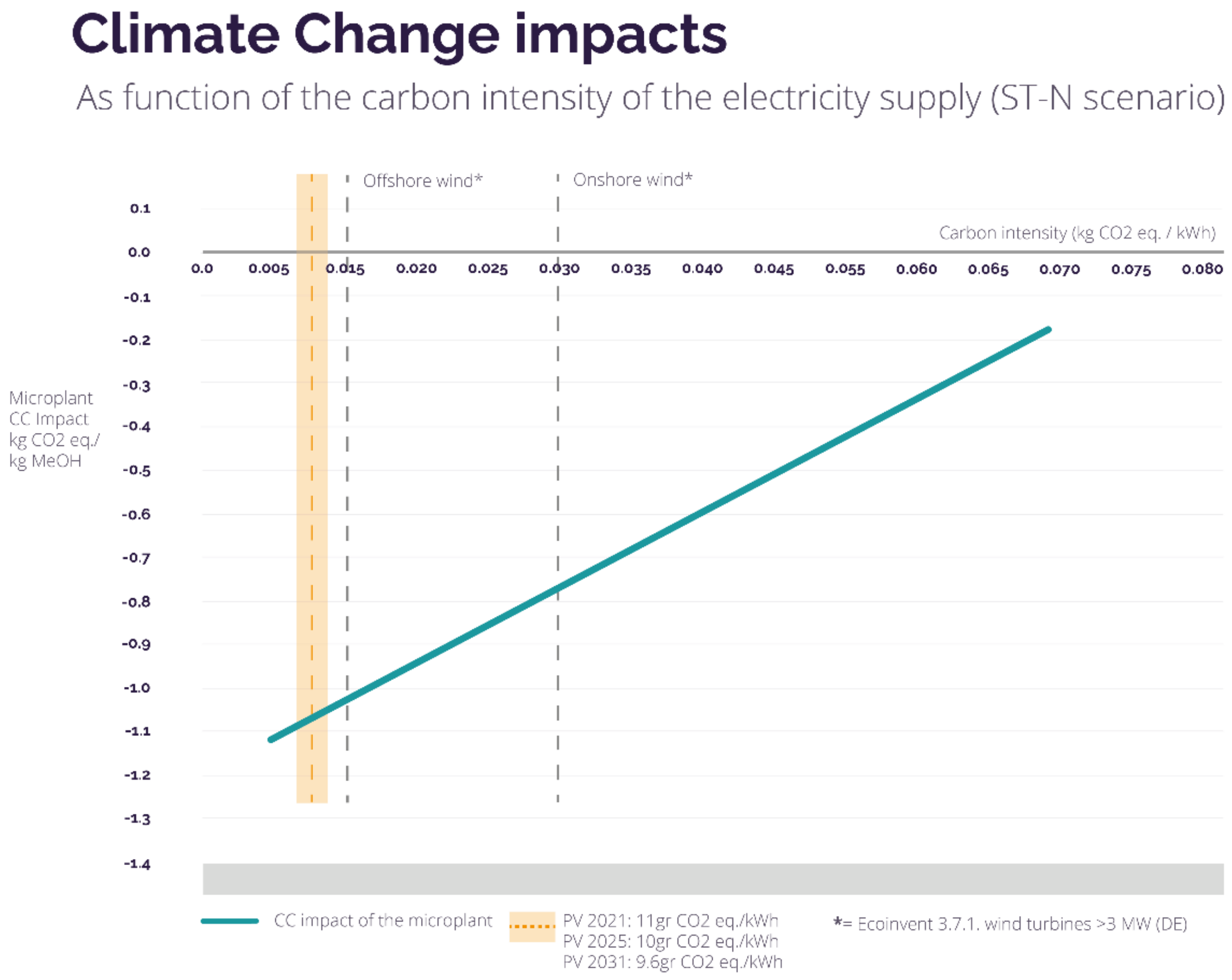


Figure 17: Climate Change impact score of the methanol produced by the microplant as function of the carbon intensity of the electricity supply

Figure 17 describes the correlation. The carbon intensities of the PV scenarios used in this study are also plotted. The correlation between the carbon intensity and the CC impact of the produced methanol can be approximated using the following equation:

$CC\ IS = 13.78 * C.I.E.\ (CO_2\ eq./kWh) - 1.22$
CC IS: Climate change impact score of the microplant
C.I.E.: Carbon intensity of the electricity supply

This means that the cradle-to-gate CC impacts of methanol produced via the microplant start becoming net-positive around an electricity carbon intensity of 88.8 grams of CO_2 eq. / kWh, which is about the intensity of the French electricity mix at the time of writing (RTE-France, n.d.). Most renewable energy technologies and especially novel photovoltaic technologies remain far below this level (Blanco et al., 2020), meaning that on the cradle-to-gate system boundary, a negative CC impact is practically guaranteed using the current approach.

7.4. *The material demand of microplant-methanol*

An additional interpretation of the significance of the microplant material demand
The impact assessment indicated that a large share of the overall impacts is caused by the upstream impacts of the demand for metals of both the microplant and the photovoltaic system. To further investigate the importance of the material demand and to highlight the material demand as potential major difference between microplant-based methanol and conventional methanol, the overall material demand is subjected to a brief further investigation in this section.

Another impact method and manual calculations for material quantification
To ensure consistent results, two methods were used to estimate the material differences between methanol from the microplant *under the short term neutral scenario* and conventional methanol. In the first method, the EDIP 2003 impact method was used in an additional impact assessment of the microplant with and without the burdens of PV electricity, compared to conventional methanol. The EDIP (Environmental Design of Industrial Products) 2003 impact method includes multiple impact factors for individual aggregated minerals, metals and some biotic resources. It contains characterisation factors for the absolute depletion of metals (i.e. use of resources 'from ground'). Because updates in this impact method are no longer published the metal demand is secondly also manually calculated using Excel data manipulation of the complete calculated life cycle inventory. Manual calculations also include the use of secondary material (i.e. metal scraps, or tailings).

Resource assessment reveals a far higher metal demand, manual calculations show smaller differences
The outcomes of the additional impact assessment using the EDIP 2003 resource impact method are visualised in figure 18. This first analysis shows that the microplant indeed should be associated with a higher demand for minerals and metals. The manual calculations consistently indicated smaller differences between the microplant and conventional methanol, though there was still no case where the material demand of conventional methanol was higher.
The smallest difference can be found for the iron demand. The manual aggregation of relevant Technosphere flows in the life cycle inventory showed that conventional methanol requires a higher input of iron than microplant-based methanol without PV burdens. If PV burdens are included however, the complete microplant system requires about 20% more iron. The manual calculation revealed larger differences for the copper demand (3.9x), Nickel (9.9x), Aluminium (8.6x), and various plastics (2-20x). Materials not shown in the chart are tin and tantalum which, due to their occurrence in electronic products, have a demand factor of around thousand x compared to conventional methanol.

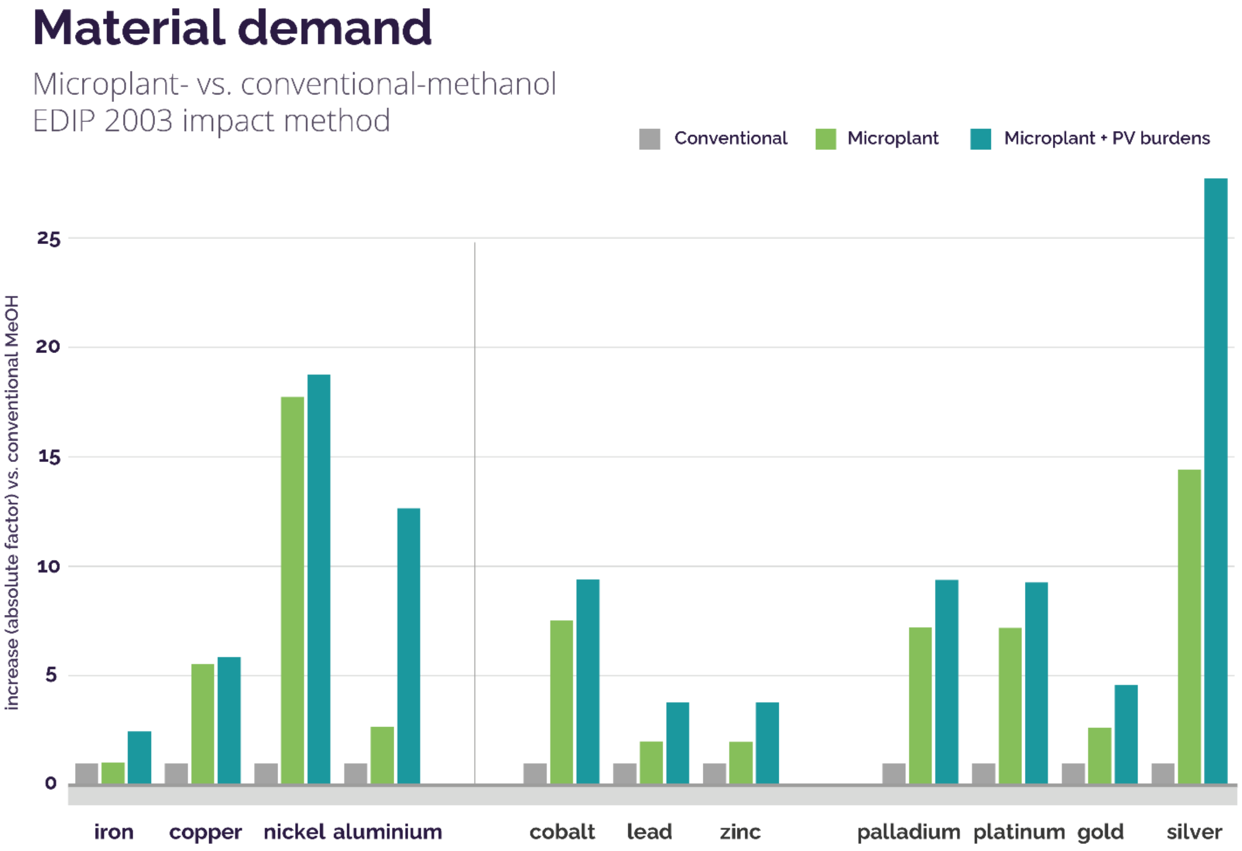


Figure 18:Mineral and metal demand of the microplant with and without PV burdens compared to conventional methanol as reference. Calculated using the EDIP 2003 impact method. Manual calculations consistently indicated smaller but still large differences. Interpretation example: The copper demand following the EDIP method is over five times as large as that of conventional methanol, using manual calculations the difference it is roughly four times larger.

This brief material assessment confirms the hypothesis that the overall material use is indeed much higher than conventional methanol, so much so that even without considering the burdens of PV electricity the microplant alone already accounts for a majority of the analysed material types. As was seen in previous interpretation steps, some specific material requirements can be connected to significantly higher impacts in categories such as acidification, eutrophication, (non-)carcinogenic effects, and respirator effects. As will be discussed later, the overall material demand is highly uncertain. The lifetime of the microplant, which is assumed to be 20 years by default, has a major influence in how the overall material demand is calculated.

7.5. *Other sensitivity analyses*

There are a multiple key aspects of the LCA that are unique to the microplant concept and which are also deemed important for the impact results as well as being highly uncertain in the current stage of the development of the microplant at Z.E.F. B.V.
Currently it is not possible to provide an appropriate single point value for either of these parameters due to the low technology readiness of the microplant concept. Yet, it is expected that the respective relevance of these parameters in the total environmental profile will be important in determining the path of further design developments. Here, these parameters will be briefly described and subjected to a sensitivity analysis. This will be done in a so-called 'window of operation' overview which describes a range of potential impacts based on variability in the parameters, thereby creating more insight about the relevance of the parameters and resulting redesign needs for the technology developers.
Momentarily, there are three parameters / aspects of the microplant system that will be evaluated;

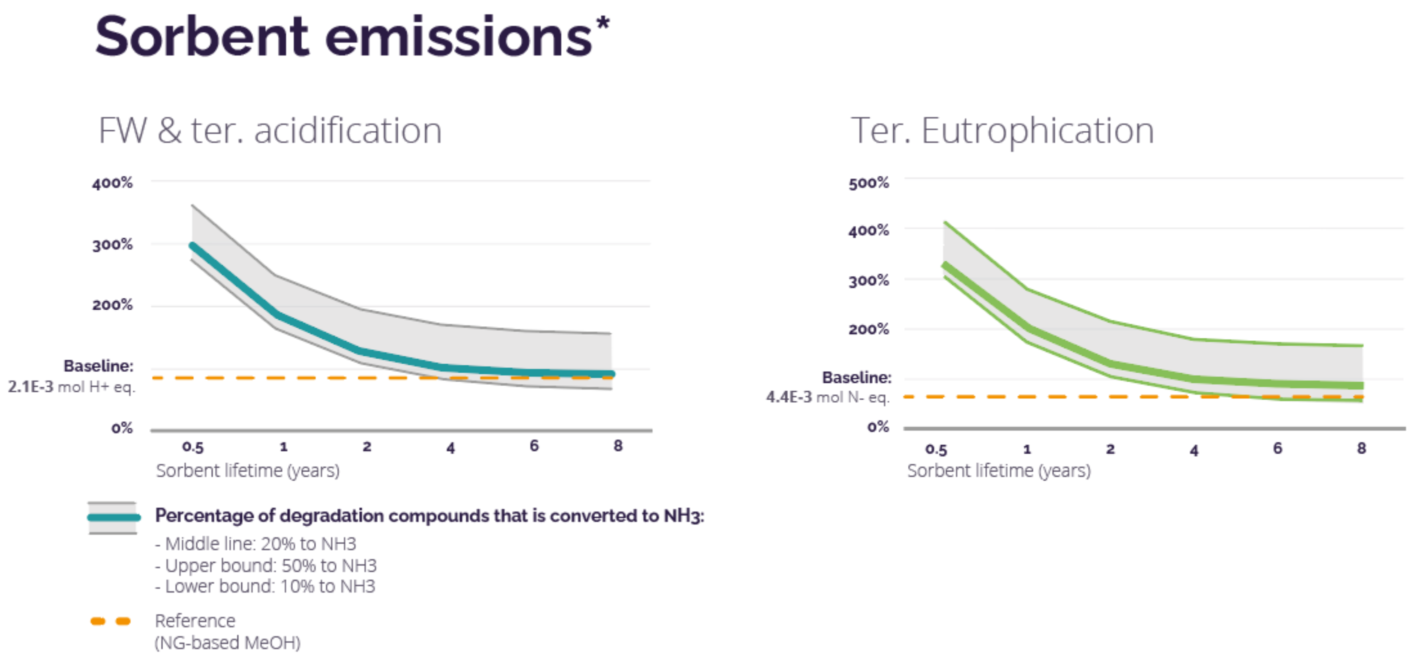
1. Degradation (Lifetime) of the sorbent
2. Ammonia emissions related to the use of an amine-sorbent in the DAC subsystem
3. Nitrogen purging in the methanol reactor
4. Hydrogen emissions

7.5.1. Ammonia emissions as result of sorbent degradation

In general it is deemed largely impossible to accurately model the direct amine-related emissions for mainly two reasons; The first is the lack of established data and literature on the specific degradation and evaporation behaviour of the sorbent. The second is that degradation and related emissions are highly context-specific (i.e. temperature, moisture, sun irradiation) adding more complexity to the modelling of degradation. To still include the potential pitfall of amine-use in the Direct Air Capture unit, an approximating approach is adopted that examines the sensitivity of the LCA model for variations in the simplified parameters that determine the emissions of degraded compounds.

An additional interview was planned with the technology developers to come up with the first set of assumptions and parameters. The most important assumption is that the range of emitted compounds was limited to just ammonia, as this is the most volatile of compounds and the most likely to exit the system (M., Singha, personal communication, n.d.). Other degradation compounds will likely be salts, which are non-volatile and are deposited as salts within the system. The added reasoning behind limiting the modelling of DAC emissions to ammonia is the fact that specific other volatile degradation compounds will not have characterisation factors in any of the weighing methods, leading to their irrelevance in the overall method of impact calculation. Additionally, the sorbent itself is expected to degrade rapidly in the atmosphere into the aforementioned degradation products (NCBI, 2021).

The ammonia emissions were approximated as being a variable percentage of the total amount of degraded sorbent (in kg). This amount of degraded compounds is then directly linked to the lifetime of the sorbent in the system, as the sorbent is replaced when the max. cyclic efficiency reaches 80% (i.e. a degradation of 20%). The resulting correlation between the lifetime of the sorbent and the amount of degradation products that form pure ammonia is visualised in figure 19. However, it should be explicitly mentioned that this approach merely serves as an approximation and discussion-tool for the impacts of direct amine-related emissions. By no means is it a realistic representation of the system in practice.



Sorbent emissions*

FW & ter. acidification

Ter. Eutrophication

Figure 19: Sorbent emissions as function of key assumption regarding the emission of ammonia from degraded sorbent

The sensitivity analysis creates a range that, depending on the eventual measurements from the prototype, depict the potential future impacts of the microplant system in the Acidification and Eutrophication impact categories. The grey lines represent the upper and lower bounds of the 'impact space', the coloured line in the middle represents the impacts as they were modelled in the base scenario. Depending on the sorbent lifetime and the degradation rate of the compounds into ammonia, the microplant can reach an acidification potential that is 3.7 times higher and an eutrophication impact that is 4.1 times higher than the base scenario. This would exacerbate the difference between methanol produced by the microplant and methanol produced via conventional pathways, leading to a clear disadvantage of pursuing the microplant concept in this particular impact category. Recommendations following from this brief sensitivity analysis will be elaborated in chapter 8.

7.5.2. Nitrogen purging in the methanol reactor

With the large volumes of air required to extract sufficient carbon dioxide and water, it is inevitable that a portion of nitrogen is co-captured. The nitrogen is then transported to the methanol reactor where it remains as there is no automatic exit route for the accumulated nitrogen. To rid the methanol reactor of nitrogen the entire content of the reactor can be purged at a set frequency. Besides nitrogen, gasses present in the methanol reactor such as hydrogen and carbon dioxide are then also vented into the ambient air. The venting of carbon dioxide does not immediately present a problem, as this was captured just moments ago in the DAC unit. Other gasses however, can act as a greenhouse gas and therefore could be a significant contributor to the environmental profile. Potential mitigation of the gasses could consist of flaring (i.e. burning) with the downside that this adds to the technological complexity of the system.

The overall purge percentage is mostly an indicator for the total conversion efficiency of the feedstocks to methanol. Naturally, a higher conversion efficiency is desirable as less energy is spent on the production of feedstocks that are not used for the production of methanol. In literature, purge percentages typically lie somewhere between 1-2% (Nieminen, laari & Koiranen, 2019; Rosental et al., 2020). Valorisation of purge gasses was investigated by some authors (e.g. Consalez-Garay et al. 2019), for example for the production of steam for other processes.

For the LCA model, the purging is simplified and modelled as a continuous exit stream from the methanol reactor of 1-5% of its total production. The required compensation by the DAC, AEC, FM, and MS subsystems to still reach the production target results in an average increase between 0.8 and 4.2% in the Climate Change category depending on the purge percentage. The direct emissions of hydrogen and carbon dioxide as part of the purge do not lead to major changes in any of the ICs. It therefore remains important to ensure that nitrogen accumulation is prevented as much as possible to limit the need for purging the valuable feed-gasses.

7.5.3. Contribution of the sorbent and its lifetime to the GWP

Per the default modelling choices, the sorbent accounts for roughly 10% of the microplant-related impacts, i.e. not the impacts related to the production of electricity for the microplant operation. There are two reasons for more closely examining the relevance of the sorbent for the impact results. For one, the relative contribution can vary significantly depending on the various parameterized inventory inputs. In addition, the choice of sorbent is one of the primary drivers for a specific DAC design and should therefore be subjected to additional scrutiny.

The total GWP impact of the sorbent is expected to lie somewhere between 11.9 and 19.9 kg of CO_2 eq./kg of sorbent. The range can be explained by the underlying allocation procedure. The lower value is retrieved if the impacts are allocated on an estimated economic basis whereas the upper value originates from full allocation to the desired sorbent. Economic allocation roughly allocates half of the impacts to the co-produced product which might be underestimate the real impacts of the sorbent due to the lower demand for this specific product. Similarly, full allocation of the impacts to the sorbent might be an overestimation due to the relatively conservative yield of the modelled production process. It is therefore assumed that the real value lies somewhere between the lower and upper value.

The production process modelled in this study assumes the formation of TEPA and co-produced HEDETA from diethanolamine, ethylenediamine, and ethyleneurea. The latter is not represented in ecoinvent and was replaced with the proxy imidazole which is a similar molecule that does not contain the additional oxygen atom. An analysis of the GWP of the sorbent production process reveals that this proxy is responsible for near to 50% of the total impact. For a follow-up it would therefore be useful to revisit the assumption made in this study and examine whether the production of ethyleneurea is comparable to the production of imidazole. Diethanolamine plays a smaller role, accounting for over 22% of the GWP impacts, whereas ethylene diamine is barely noticeable at all in the environmental profile of the sorbent.

As previously discussed it is assumed that no sorbent is recovered due to the homogenous nature of the mixture which would likely require separate processing for partial recovery of the non-degraded sorbent. The end-of-life phase of the sorbent thus consists solely of transport and treatment in the form of incineration with energy recovery, accounting for 21% of the sorbent GWP impacts.

The relation between variation in the sorbent lifetime and the total GWP category of the produced methanol (kg CO_2 eq. / kg MeOH) is visualised in figure 20. The contribution of the sorbent to the total GWP impacts is not large enough to significantly impact the microplant's performance in relation to conventionally produced methanol. Yet, under the current pessimistic short term scenario the sorbent is expected to require replacement every six months, which results in a maximum increase GWP of 10%. The efficiency of sorbent use within the DAC unit thus remains an important performance indicator.

Strikingly, the sorbent lifetime and resulting additional sorbent production is far more significant in the marine eutrophication category. A reduced lifetime of 1 year from the default 4 would increase the marine eutrophication score with approximately 15% due to the eutrophication potential of TEPA's primary products. A similar but smaller effect can be observed in the ionising radiation category (~5%).

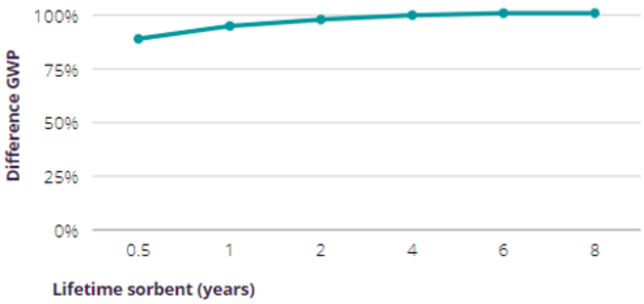


Figure 20: Sensitivity of the microplant LCA with regards to variations in the lifetime of the sorbent and diluent.

7.5.4. The potential GWP of hydrogen emissions

Some researchers argue that hydrogen might function as an indirect greenhouse gas (GHG) by reacting with hydroxyl radicals (Derwent et al., 2020). Hydroxyl radicals are an oxidizing agent in the troposphere and their reduction contributes to an extended lifetime of GHGs such as methane. Consequently, hydrogen emissions also indirectly influence ozone concentrations, potentially adding to the depletion of the ozone layer in the stratosphere. The influence of hydrogen emissions in the ozone depletion category are not likely to be relevant, as this is one of the categories where the impact of conventionally produced methanol is far greater. The global warming potential however, might be more relevant to the microplant's environmental profile and its position in relation to other low-carbon methanol production pathways. Derwent and colleagues estimate that the global warming potential of hydrogen lies around 5 (+/- 1) kg CO_2 eq. over a 100-year time period (Derwent et al., 2020). Significant emissions of hydrogen in the methanol production chain might therefore partially mitigate the beneficial effect of CO_2-based methanol. Still, the global warming potential of hydrogen is highly uncertain (Weger, Leitau & Lawrence, 2021) and has only been studied by a few researchers.

To test the potential influence of direct hydrogen emissions, the emissions are simulated by replacing hydrogen emissions by carbon dioxide emissions with the appropriate global warming potential of 5 kg CO_2 equivalent. On average, the methanol reactor emits about 13 grams of H_2 per kg of MeOH, assuming the potential GWP of hydrogen, this is about equal to the emission of 65 grams of CO_2 per kg of MeOH. In the total impacts under the ST-N scenario this would lead to an increase of 6.3%. This number would increase significantly if a GWP would also be considered for purged gasses. In fact, the continuous emission of 2% of the feed gasses would be enough to reduce the negative CC impact score to zero on a cradle-to-gate basis.
However, as previously addressed, the GWP potential of hydrogen is highly uncertain. The influence of this consideration on the conclusions is discussed in chapter 8.

08 Cross-study Analysis

1. Cross-study analysis: Introduction
2. Literature overview: Technological variation
3. Literature overview: Methodological variation
4. Results: Climate Change Impacts
5. Other impact categories in CO_2-based methanol studies
6. Comparison of key process parameters
7. Cross-study analysis: Discussion

8. Cross-study analysis

8.1. *Introduction*

Comparing LCA results with results in comparable LCA literature
The main purpose of this chapter is the comparison of the retrieved results from the LCA of the Z.E.F. methanol microplant with reported LCA scores in relevant literature. Normally this is done by including an alternative in the LCA approach where the entire alternative product system is modelled with the same detail as the primary product system. This approach is not followed in this thesis, mostly due to the large variety between available life cycle inventories and data of low-carbon methanol production (as explained by Artz et al., 2018; Thonemann, 2020). Modelling an alternative would therefore require a subjective choice regarding the performance of the alternative whereas this is an area of great uncertainty. The result could lead to potential judgement errors with large consequences for the overall assessment of the microplant.
Instead of modelling the alternative within the LCA model, it is therefore argued it would be better to consult recent LCA literature regarding CO_2-based methanol technologies; both *to reach a better understanding of the aspects that determine their sustainability* and *to (cautiously) sketch out their relation to the microplant concept*. A so-called 'cross-study analysis' can highlight potential shortcomings or merits of the microplant and its environmental profile. In turn, this exercise attempts to answer the last sub-question; *"How do the results of the LCA in this study relate to the results found in LCA literature on comparable methanol production technologies?"*

Article selection to find comparable CO_2-based methanol LCA studies
The initial filtering of the literature search results resulted in approximately 80 papers published between 2015 and 2021 that assessed the environmental impacts of both *CO_2-based methanol* and *biomethanol* types. The analysis of *biomethanol* papers has been excluded entirely in this version of the report, and can be found in appendix H. The brief overview of insights from this analysis is included at the end of the chapter.
A relatively large share of the initial papers were not deemed suitable for the purpose of this chapter for a variety of reasons, and were therefore excluded from the collection. Some papers for example, adopted a consequential instead of attributional modelling approach (e.g. Qahtani et al. 2020; UUsitalo et al., 2017). Others mainly relied on older LCAs without much new added data, abstained from correctly following the LCA methodology, or reported impacts in non-conventional ways (e.g. Ravikumar et al., 2020; Consalez-Garay, 2019). An identified keystone paper is the work by Artz et al. (2018) which was often cited by papers found in the initial search. Artz and co-authors in turn used data by Hoppe et al. (2018), Pérez-Fortes et al. (2016) and Sternberg et al. (2017), each of which were also often referred to in newer papers.
From the initial selection of 80 papers, 18 papers assessing CO_2-based e-methanol remained. Combined, these studies assess 38 alternative product systems, of which the majority is deemed useful for this analysis.

8.2. *Literature overview: technological variation*

The full overview of the cross-study analysis can be found in appendix G. This section will only briefly discuss the literature and the variation of the assessed systems.

CO_2-based e/f-methanol and its variation in collected LCA works
First and foremost the main source of variation between the collected studies can be found in the composition of the production chains. As summarised in chapter two, the production chains are mostly determined by the number of processing steps and the sources of feedstocks delivered to the production chain. Out of the 18 CO_2-based e/f-methanol LCAs, all considered direct hydrogenation (i.e. one-step approach) either as the primary product system (15/18) or as an alternative (3/18). Most authors explained that the reason for the focus on direct hydrogenation is its thermodynamically favourable position with respect to syngas conversion (i.e. two-step approach). Other arguments pointed at the strongly increasing research into direct hydrogenation of CO_2 for value-added products and the already existing pilot projects showing its technological feasibility.
Three out of 18 LCAs considered syngas conversion in addition to direct hydrogenation. Artz et al. (2018) used existing literature to assess the impact of syngas produced by rWGS, Co-electrolysis, and solar-thermal disassociation. Adnan & Kibria (2020) model the electrolysis of CO_2 in addition to a low-TRL direct synthesis to

methanol. Two out of the 18 LCAs include the electrochemical conversion of CO_2 to CO and methanol using solid oxide electrolysis cells (Nabil et al. 2021; Rumayor et al. 2021). The photocatalytic direct conversion of CO_2 to methanol was only assessed in a single study by Ryoo et al. (2021).

Secondly, In terms of energy use and feedstocks it can be seen that the majority of studies used wind energy as main supplier of electricity (14/18), next is electricity from local grids (8/18), photovoltaic electricity (7/18), and nuclear electricity (4/18). Heat was mostly sourced from natural gas (9/18) though this was often coupled to heat integration to minimise heat-related impacts. Two studies assumed heat from power-to-heat technologies, another two considered waste heat from other industrial processes, only one study assumed solar thermal as main heat source.
The analysed product systems most often relied on feedstock-CO_2 from point-source capture (12/18) and CO_2 from industrial chemical processes (4/18). Direct Air Capture was not often included (3/18), with the lack of reliable data as the most reported reason. Hydrogen was most often produced in electrolysis cells with about an equal preference for PEM and AEC, only a few studies also considered other cell types such as SOEC or fossil routes via steam methane reforming.
The included studies combined these 'building blocks' that make up CO_2-based methanol production chains into various designs with rarely matching chains between studies. For an overview of the studies, the reader is referred to appendix G.

8.3. *Literature overview: methodological variation*

Any literature-based comparison would be illogical if no attention would be given to the methodological foundation of the screened papers. Especially for the case of CCU projects, matters such as the system boundaries and approaching multifunctionality determine for a large part the impact results. This section briefly discusses the methodological and technological choices in the screened papers with the aim to better support the comparative discussion. A more elaborate overview is provided in the supplementary materials.

System boundaries & three found strategies for carbon accounting
With exception of the frequently occurring (11/18) mismatch between the temporal context of the foreground and background system (as van der Giesen et al. (2020) identified), no major remarks can be made about the goal and scope definition of the collected studies. In terms of system boundaries, nearly all studies assumed a cradle-to-gate approach with the exception of Biernacki et al. (2018), Rosental et al. (2020) and Fernández-Dacosta et al. (2019) who also explicitly addressed the end-of-life of the produced chemicals in a cradle-to-grave approach.

Besides system boundaries, the methodological treatment of feedstock CO2 appears to be a major source of variation between studies. Practically, this leads to 1) Differences in the provision of capture-credits to the CO2 feedstock, and 2) the inclusion or exclusion of carbon capture processes from the product system. Various strategies to deal with these two points can be identified.
The first strategy, which is followed by most papers, circumvents part of the complexity of CCU LCAs by assigning a set negative CC impact score to the CO2 feedstock based on earlier reports or estimations. In essence, this leaves the CCU part of LCA to the work by other authors and instead allows the LCA to focus more on the utilisation part of the CCU system. In the reviewed studies, assigned CO2 feedstock CC impacts vary between -0.701 and -1.0 kg CO2 eq. / kg CO2. Because these value are based on literature estimates, they tend to include burdens of the capture process (Müller et al., 2020b).
In the second strategy, authors partially or fully model the capture process in their LCA. A choice then needs to be made about what process-burdens are allocated to the CCU system, and which to the system that emits the CO2. Besides, this approach still leaves the issue of assigning credits for temporary sequestration of CO2 in the CCU system. Under the second strategy however, this can be approached more comprehensively by stating which processes are included in the system boundaries and whether carbon credits (-1 kg CO2 eq.) are considered or not. Only a couple of studies used this second strategy, but it did allow them to discuss the wide range of impact categories beyond Climate Change that would not have been possible under the first strategy.
The last and third strategy, is the expansion of the system boundaries to entirely encompass both the CCU system and the emitting system. This is by far the most resource intensive strategy but it does allow authors

such as Eggeman et al. (2020) and Fernande-Dacosta et al. (2019) to elaborately discuss the role of carbon accounting in the assessment of specific cases, which is generally recommended (Ramírez Ramírez et al., 2019). Knowledge of these three strategies of carbon accounting in LCA is necessary for the interpretation of the results in the next section.

Foreground data collection – limited experimental results
Of particular importance to this exercise is the origin of the data that describes the CO_2-based r/f-methanol and bio-based methanol production systems. For the modelling of the methanol synthesis process and carbon capture process, an equal preference in the screened papers was found for computer simulation of key processes with dedicated software, and the manual calculation. Sticking to the hierarchy of LCI data collection from Parvatker & Eckelman (2019), only a couple of papers actually used data from pilot projects or lab-experiments and most used stoichiometry and proxies to compile the data for the foreground system, resulting in a lower overall data quality.
Heat and electricity inputs for all processes were almost never modelled in the foreground and instead came from background databases. As demonstrated in this study, this can lead to overestimation of impacts.
Only a few authors actually considered material and energy inputs for the construction of carbon capture and methanol synthesis plants (e.g. Rosental et al., 2020; Biernacki et al., 2018; Meunier et al., 2020). Even fewer included major transportation processes for key material inputs and exchanges (e.g. Chen et al., 2019; Fernandez-Dacosta et al. 2019). Papers furthermore rarely discussed practical matters such as operational equipment efficiency, the effect of intermittency of renewable electricity, and maintenance.

Impact assessment
All papers included the Climate Change impact category in the impact assessment with the exception of the work by Consalez-Garay (2019) who used endpoint indicators in their assessment. Only seven out of the 18 studies on CO2-based r/f-methanol included other relevant environmental impact categories regarding impacts on ecosystem quality or human health. Another four included indicators regarding the efficiency of used energy and the use of fossil resources. Bio-based methanol studies tended to include the entire environmental profile with seven out of the total of nine studies. The impact methods used by the authors to calculate the impact indicators were most often the ReCiPe (7/27), CML 2001 (5/27) and ILCD methods (4/27).

Overview
As can be deduced from this section, the variation between studies is large. Still, some consistencies can also be found, for example in the approach to the modelling of the foreground system, the use of background databases, LCA software, and impact assessment methods. With caution, it should therefore be possible to map the results of these papers and assessing the relation of the LCA performed in this study to the reported results.

8.4. *Results - Climate Change impacts*

In this section, the Life Cycle Impact results of the reviewed papers will be placed in perspective to the impact results of the Z.E.F. methanol system. This will be done in a side-by-side manner, meaning that besides impact method harmonization for some specific cases, no additional calculations are performed. The goal of this section is both to screen the LCA literature of low-carbon methanol production on technologies that might outperform the ZEF microplant, as well as attempting to identify potential trade-offs or impact results that deviate from what has been reported before in comparable LCAs.

8.4.1. Climate Change impacts – CO_2-based r/f-methanol

The previous sections have indicated that comparability in published studies on CO_2-based methanol and biobased methanol tends to be challenging. The many sources of variation in both the methodology and the compilation of the life cycle inventories cause discrepancies that disrupt the potential for comparison. Therefore, an attempt is made to reflect important findings considering these sources of variation together with the impact results found in literature. The aim here is to provide more easily interpretable results. Still, by no means is it the goal of this section to force conclusions or underestimate the challenge of comparing LCA publications. The difficulty of comparing CCU LCAs is once more confirmed by this exercise.

One of the most often cited main contributors is the energy supply, more specifically its carbon intensity (kg CO_2 eq. / MWh or MJ). Three sub-categories can be compiled, 1) Systems that fully rely on renewable energy, 2) systems that combine renewable and fossil energy, 3) systems that are dependent on fossil energy sources. To enable better interpretation, the reported results are divided based on their respective energy systems.

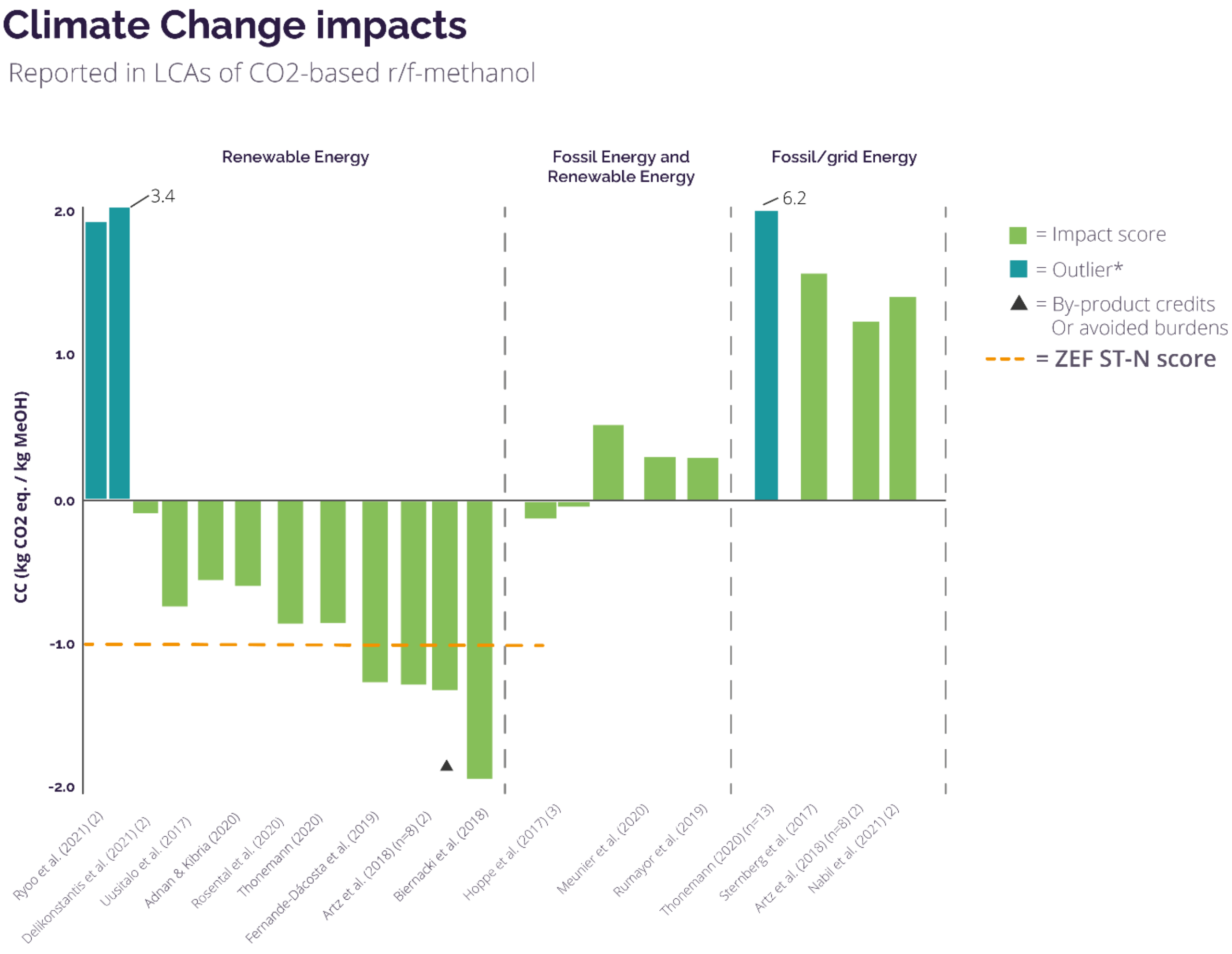


Figure 21: Climate change impacts reported in analysed literature.

Figure 21 provides a global overview of the position of the Z.E.F. methanol production concept in relation to technological competitors from published literature. The reader is advised to be careful with the interpretation of the figure, comparison of unharmonized LCA results from separate studies should never form the foundation for drastic conclusions.

Impacts in fact seem to stick to the energy system hypothesis

A first observation that can be made is that the reported CC impacts of systems differs strongly between used energy types (i.e. renewable/fossil). There seems to be truth in the often mentioned hypothesis that the CC score of CCU methanol is largely determined by the carbon intensity of its energy supply. Some outliers can be identified that are caused by the provision of avoided burdens (e.g. Biernacki et al., 2018; Eggeman et al., 2020), or potential errors in LCI data (Ryoo et al., 2021).

Microplant impacts are in line with reported literature results

Regardless, the figure serves its purpose by showing that there are no large discrepancies between the CC impacts calculated in this study and the impacts reported in literature. In other words, using the limited data available, the Z.E.F. system seems to perform comparably in the CC category. Compared to CO_2-based methanol production routes using only fossil energy or a mix of renewable and fossil energy, the Z.E.F. system performs significantly better, making it less likely that any change in methodology or assumptions could turn the tide in favour of these competing systems. For the direct competitors, it is impossible to say whether or not changes in methodology could compromise the current position of the Z.E.F. system. Only a few studies actually reported more favourable CC impacts (e.g. Artz et al., 2018, Fernande-Dácosta, 2019; Thonemann, 2020). These studies are briefly elaborated.

A very low CC impact can often be explained by looking at the study's assumptions
In their best case scenario Artz et al. (2018) reported CC impacts between -1.23 and -1.28 kg CO_2 eq. / kg MeOH for the direct hydrogenation and syngas conversion of CO_2. These results are close to the minimal achievable results considering the stochiometric maximum sequestration potential of methanol (-1.37 kg CO_2 / kg MeOH) under the condition that avoided burdens or credits were not considered. The harmonization procedure followed by the authors removed most of the large variation between the assessed studies and the authors concluded that no significant difference between various methanol production routes could be identified regardless of major differences in process parameters. It is therefore more likely that the reported impacts are the result of the general methodological approach (as discussed in section two of this chapter). Indeed, Artz et al. consider the feedstock CO_2 to have a carbon intensity of -1 kg CO_2 eq. / kg CO_2 and do not take into account the impacts of potential capture processes. Additionally, the carbon intensity of the energy supply is very low, 0.0025 kg CO_2 eq. / MJ of heat and 0.0088 kg CO_2 eq. / kWh of electricity. The combination of these two assumptions produces impact results that might be too optimistic even for a futuristic best case scenario.

Cradle-to-gate results deduced from the work by Fernande-Dácosta et al. (2019) came to a range between -1.17 and -1.23 kg CO_2 eq. / kg MeOH depending on the applied carbon accounting methodology. However, for the scenario that includes carbon capture deeper analysis of the contribution of individual processes reveals a low energy intensity of the capture process. In addition, some credits seem to be given to the production of oxygen by-product from water electrolysis although this is not transparently reported. The authors also state that the inclusion of infrastructure would reduce the benefit of the CO_2-based methanol significantly.
A study with a comparable impact score to the microplant was performed by Thonemann (2020), which consisted of collecting 13 reproducible LCA studies. The result is a cradle-to-gate impact score ranging between -1.05 to -0.5 kg CO_2 eq. / kg MeOH with a mean of -0.86 kg CO_2 eq. / kg MeOH. Thonemann considered more realistic carbon intensities for heat and electricity supply with an estimated 0.105 kg CO_2 eq. / MJ and 0.03 kg CO_2 eq. / kWh respectively. Some energy and material requirements for the capture of carbon dioxide were also considered based on earlier work by Thonemann and colleagues.

DAC studies are rare and do not show large differences with point source capture
Only a few studies assessed Direct Air Capture. Hoppe et al. (2018) included DAC in their analysis but considered natural gas to supply the DAC unit with heat, leading to higher impacts of methanol from DAC-CO_2 than from PS-CO_2 (~0.5 vs ~-0.1kg CO_2 eq. / kg MeOH). Sternberg et al. (2017) also include DAC-CO_2 as feedstock but only as input for the determination of an average GWP for the CO_2 supply combined with point source capture and other sources. The authors also use fossil-based heat for all heat demand, leading to larger impacts than conventionally produced MeOH. Only Rosental et al. (2020) included DAC combined with renewable electricity and heat from wind turbines in a 2010 and 2050 scenario. On a cradle to gate basis, the systems modelled by Rosental et al. result in CC impacts between -0.80 and -0.912 kg CO_2 eq. / kg MeOH depending on the 2010 or 2050 scenario.

Overall, the study by Rosental is the most comparable to the LCA performed in this study due to the use of future background scenarios, inclusion of infrastructure and transport, the type of CO_2 supply, and the use of renewable energy for all key processes. In addition, the electrical energy and heat demand for CO_2 capture, hydrogen production and methanol synthesis are similar or lower to the assumptions in this study. For the 2050 scenario for example, the total heat and electricity input for CO_2 capture is around 2.6 kWh / kg CO_2, for hydrogen it is 41 kWh / kg H_2 and for methanol synthesis it is around 0.8 kWh / kg MeOH. Even still, the 2050 DAC scenario 'only' leads to a negative cradle-to-gate impact of -0.912 kg CO_2 eq. which is about as much as the short term pessimistic scenario of this study. The reason for this discrepancy can be found in the contributions, which will be discussed in the next section.

Varying relevance of certain processes in reported contributions
To see whether impact hotspots in the reviewed literature align with the hotspots in this study, the reported contributions are briefly discussed. Such analysis was not performed equally in all papers, meaning that

variation exists in whether or not the total impacts are divided based on foreground process contributions (CO_2 capture, synthesis) or general background process contributions (i.e. electricity, steam). It is therefore not possible to access the contributions of the CC impact category on equal levels.

Besides the perhaps obvious role of hydrogen production and the impacts of energy supply, it is more interesting to look at what authors have to say about other contributions in their foreground systems. Meunier et al. (2020) for example found that the regeneration of the solvent for CO_2 capture was almost as relevant for the total CC impact as hydrogen production due to the high heat and electricity demand for desorption. The particular importance for this process was not found elsewhere in literature, at least not in the same sense as reported by Meunier et al.

In addition, direct emissions from the combustion of inert flows for heat integration played a significant role in Meunier's LCA model. Similar importance for direct emissions was found by Rosental et al. (2020). Due to the difference in the nature of the CO_2 in the DAC and PS alternatives (i.e. regarding allocation choices) direct emissions were much more relevant for point source capture systems then direct air capture systems, approximately leading to 26-68% of the total emissions.

Distillation of the methanol and water mixture to form 99% pure methanol was not considered as a very important process by most papers though strangely Nabil et al. (2021) point towards this process as main contributor of the poor performance of CO_2-based methanol in their study. According to Nabil et al., the distillation needs 26.43 kWh / kg of energy and thereby forms 62% of the total energy demand for that production route, leading to considerable impacts from upstream electricity generation processes. Many other studies considered using waste-heat from hydrogen production and mostly methanol synthesis to supply either (or both) the CO_2 capture and the distillation process of its heat demand. Perhaps this explains why distillation is not regarded as important process in most studies, though data is lacking to confirm whether this is the case.

Interestingly, the research by Rosental et al. was one of the few to include full infrastructure which proved to be very significant for the DAC system and the primary reason that it was outperformed by the point source system. The full infrastructure requirements for the carbon capture system account for about half of the total CC impacts and are more impactful than use-phase related impacts (i.e. energy, heat). It is not clear why the infrastructure impacts in the study by Rosental et al. are that high.

8.5. *Other impact categories – CO_2-based methanol*

The challenge of mapping other impact categories

The reporting of the CC impact of biobased and CO2-based r/f-methanol allowed a mapping of the competitive landscape in terms of environmental performance. The mapping exercise was mainly possible as result of the fact that CC impacts are always reported in LCAs. Unfortunately, most studies tend to exclude all other major impact categories that could highlight important trade-offs. Only Thonemann (2020), Rosental (2020) and Meunier (2020) considered important ecosystem quality and human toxicity impact categories, be it using different impact families (ILCD, CML, and ReCiPe respectively). Mapping the position of the ZEF microplant concept in relation to its competitors for impact categories other than climate change is therefore impossible. Instead, the results of this study are compared with only the results reported by Thonemann and Rosental. Again, this section is approached carefully in the knowledge that comparing unharmonized LCA studies is far from what is considered best practice amongst LCA scholars.

Thonemann (2020) for comparison and as representation of the industry average
The comparison with the results published by Thonemann is deemed relatively acceptable due to the use of the same impact method (ICLD 2016 vs 2018), similar database (ecoinvent v3.5 vs ecoinvent 3.7), transparent reporting, available LCI, and comparable energy and material carbon intensities to the LCA performed in this study. The value of Thonemann's research is that it provides an average technological performance based on 13 reports of CO_2-based methanol production, the disadvantage is that it only paints a picture of the environmental performance in the specific case of electricity production from wind power and heat delivery from average processes in the chemical industry. While considering these critical points, the work by Thonemann could cautiously be seen as a representation of CO_2-based methanol production in Europe based on currently available knowledge (i.e. 2020).
Besides Thonemann's LCA, other impact category results from the LCA study by Rosental et al. (2020) are also considered because this particular study includes Direct Air Capture modelled after the Climeworks DAC system. The study furthermore includes future background scenarios and takes into account infrastructure requirements and transport, making it one of the more comprehensive LCI's of all assessed works.

Ecosystem quality and Human Health

Side-by-side non-harmonized LCA comparison of average CO_2-based methanol production and ZEF methanol

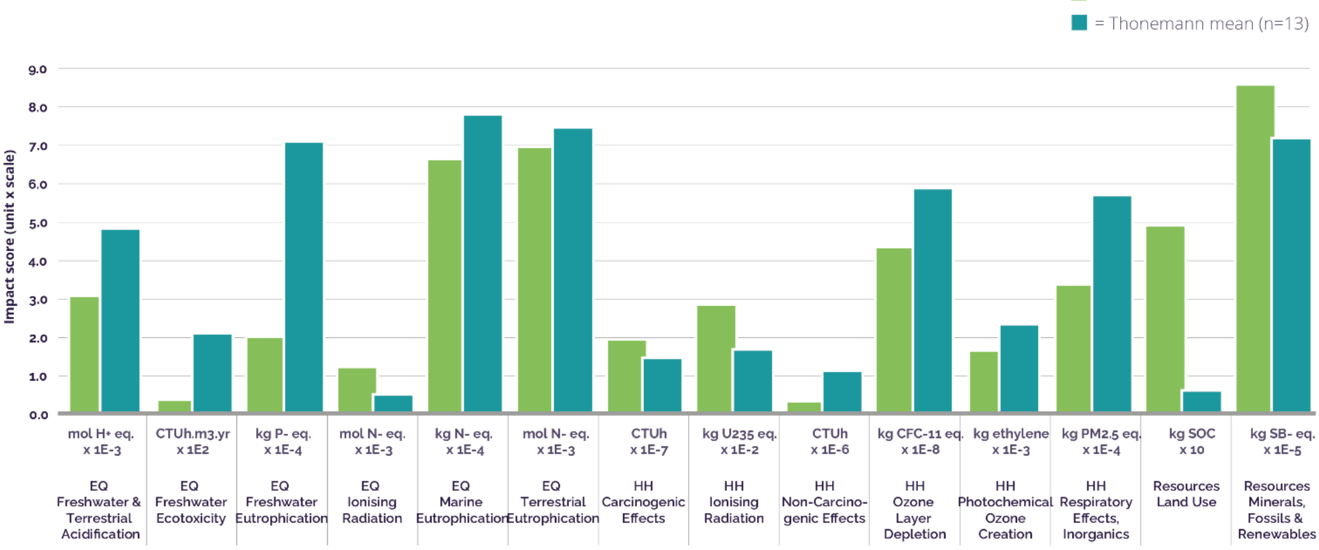


Figure 22: The impact results following the ILCD 2016 impact method. Methanol via the microplant in side-by-side comparison to the results of the harmonization study of Thonemann (2020)

Following the ILCD 2016 impact method, Figure 22 displays the impact results reported by Thonemann (2020) side by side with the impact assessment of the Z.E.F. microplant. Again, differences between the systems never exceed an order of magnitude. Larger differences in favour of the Z.E.F. microplant can be seen in the EQ freshwater ecotoxicity, EQ freshwater eutrophication, HH non-carcinogenic effects, and HH respiratory effects inorganic impact categories. Thonemann's average results for CO_2-based methanol outperform the Z.E.F. system for the ionising radiation, land use, and resource use impact categories. Thonemann attributes the relatively high ecotoxicity score to the upstream processes related to wind power, more specifically copper and other major material inputs. Interestingly, the direct NH3 emissions of the microplant appear not large enough to counteract the difference between the two systems in the acidification and eutrophication ICs. In the microplant scenario for this purpose, the NH3 emissions were set to the standard assumptions; 20% of the total degradation products produced in the DAC unit. It is expected that the difference in these ICs between the systems is caused by the reliance of Thonemann's LCI on heat produced by average processes for the chemical industry. This likely performs worse in the acidification and eutrophication ICs compared to the heat produced by PV for the microplant, though this can not be fully confirmed from the available data.

An obvious difference between both product systems is land use. The Z.E.F. system occupies a large amount of land for the solar panels; approximately 20 square metres per microplant. A more interesting result is the

Minerals, Fossils & Renewables IC where the microplant system performs less favourable compared to Thonemann's median results. The resource use by the microplant is relatively high due to the inclusion of electronic parts in the LCI and the upstream material inputs for the photovoltaic system. Together, this causes a higher depletion score than what is caused by the wind power chain in Thonemann's LCA.

Other impacts of a DAC based system reported by Rosental et al. (2020)
The work by Rosental et al. (2020) is compared with the results in this study under the CML impact method, including the Acidification, Eutrophication, and Ozone Depletion ICs. It is striking that although the methodological and technological choices of Rosental et al. are similar to the LCA in this study, a difference in order of magnitude can be seen in the Ozone Depletion category. Rosental's DAC-based methanol has a ODP score of 1.00E-6 kg CFC-11 eq. versus the 4.30E-8 kg CFC-11 eq. of ZEF-methanol, roughly a difference of a factor 250. Rosental et al. (2020) explain that the high Ozone Depletion Potential is caused by the CO_2 adsorbing material in the DAC unit, which is modelled by means of a proxy using the ecoinvent database. It is therefore not a valuable metric for the comparison of the two systems as it cannot be assumed that the ODP would indeed be this high for the DAC unit in practice. In the acidification potential category, the ZEF system has roughly the same score as the 2010 DAC-based methanol scenario reported by Rosental. In the 2050 scenario however, Rosentals system starts to perform significantly better (1.30E-3 kg SO_2 eq. vs 2.57E-3 kg SO_2 eq.). In the eutrophication potential category the difference between the ZEF and DAC-based system is smaller in all scenarios (avg. 9.0E-4 vs. 10.0E-4 kg PO4 eq.).

Overall, the impact results of CO_2-based r-methanol reported in the harmonization study of Thonemann and the DAC-based methanol study by Rosental et al., show no large differences from the results of the LCA performed in this study. The differences that remain can likely be attributed to the electricity generation processes for the case of Thonemann, the differences in the study by Rosental are more likely the result of the optimistic modelling of the 2050 background scenario. With the limited certainty that comes with this type of cross-study analysis, no major trade-offs could be identified.

8.6. *Comparison of process parameters*

The overview of the CC and other impacts of CO_2-based methanol and bio-based methanol systems in the previous section gives an initial overview of the position of the microplant in relation to these reported impacts. Yet, it should be clear that many of the underlying parameters that determine the impacts are far from similar between studies. Examples are the carbon intensity of the electricity supply and in/exclusion of infrastructure or transport. It could therefore be possible that the favourable position of the microplant-based system is entirely the result of a the low CC impact of the energy delivered to the system. To rule out the role of parameters such as electricity carbon intensity, a full technological comparison should be performed. This however, is beyond the scope of this research project. Instead, the available process data can be obtained from the assessed papers to shed more light on the difference between methanol production systems. With regards to the available resources, only CO_2-based methanol projects are considered. Data is obtained from individual studies and the harmonized LCI study by Thonemann (2020).

An emphasis should be put on the energy demand for methanol synthesis and the total energy demand. Some studies either did not include the production of feedstock CO_2 and H_2 in their systems, or did not report the key process data of these processes. Instead, the total energy demand was often provided in the papers which is why papers such as the one by Kalbani et al. (2016; as included by Artz et al., 2018) are still included. Another good metric to compare the performance of the systems is the conversion efficiency of the feedstocks into the desired product. In the table below, the conversion efficiency describes the percentage of feedstock into the methanol reactor that is converted to useful products after distillation.

*Table 16: key performance data of co2-based methanol systems. Total energy demand includes hydrogen production, carbon capture & compression, methanol synthesis, and distillation. *= conventional purge*

Data origin	*H_2 Eff.*	*CO_2 Eff.*	*Energy (kWh -no steam)*	*Total energy demand (kWh)*	*comment*
ZEF microplant	97%*	97%*		16.26-13.12	Short term pessimistic to optimistic
ZEF microplant	97%*	97%*		14.29-11.67	Medium term pessimistic to optimistic
Aresta et al. (2002)	100%	100%	11.33	11.70	From Thonemann (2020)
Biernacki et al. (2018)	99%	98%	10.89	11.34	From Thonemann (2020)
Kim et al. (2011)		75%	2.70	4.24	From Thonemann (2020)
Meunier et al. (2019)	93%	95%	11.60	12.03	Not considering heat integration
Sternberg & Bardow (2015)	96%	96%	12.22	12.64	From Thonemann (2020)
Sternberg et al. (2017) (1)	96%	96%	12.28	12.71	From Thonemann (2020)
Sternberg et al. (2017) (2)	93%	93%	12.02	12.46	From Thonemann (2020)
Sternberg et al. (2017) (3)	100%	100%	11.17	11.94	From Thonemann (2020)
Uustitalo et al. (2017)	99%	100%	11.88	12.29	Not considering heat integration
Fernández-Dacosta et al. (2019)	94%	95%	11.28	12.64	From Thonemann (2020)
von der Assen et al. (2015)	100%	100%	11.68	12.70	From Thonemann (2020)
Rosental et al. (2021) (DAC)	93%	95%	10.35	13.09	DAC - Not considering heat integration
Rosental et al. (2021) (PS)	93%	95%	9.58	10.84	PS - Not considering heat integration
Nabil (2021) (one-step)	94%	98%	52.51	52.51	Electrochemical
Nabil (2021) (two-step)	94%	98%	48.27	48.27	Electrochemical
Rumayor (2019) (DH)	100%	99%	11.90	11.90	Direct hydrogenation
Rumayor(2019) (ER)	85%	99%	50.50	50.50	Electrochemical
Hoppe (2018) (DAC)	99%	100%	12.01	12.19	Direct air capture
Hoppe (2018) (PS)	99%	100%	11.89	11.89	Point source capture
Pérez-Fortes (2016)	94%	94%	10.17	10.29	From Artz et al. (2018) Without carbon capture (high purity)
Kalbani (2016)				24.61	From Artz et al. (2018) Direct hydrogenation
Kalbani (2016)				12.61	From Artz et al. (2018) Electrochemical (SOEC)

The table reviews some key technological parameters of the papers that populate the results CC impact chart of figure 21. For a broader overview of LCI data the reader is referred to appendix I.
The ZEF system, as modelled in the LCA in this research, shows average CO_2 conversion efficiency compared to the other papers. This remark needs to be made cautiously, as the variation in reporting styles between papers is inherently vulnerable to interpretation mistakes. The CO_2 conversion efficiency is calculated by dividing the stoichiometric CO_2 consumption of MeOH production by the CO_2 intake reported in the process data of either the CO_2 capture process or the total methanol synthesis process. The CO_2 conversion in the table can therefore represent the conversion efficiency of the methanol synthesis process (including CO_2 compression), or this process in combination with the efficiency of the CO_2 capture process. The latter is likely the case in studies of point-source capture whereas it is certain that all systems reported by Thonemann (2020) describe the efficiency at the input of the reactor. Still, it does provide an initial metric to compare the performance of reported systems.

Hydrogen efficiency is about as variable between studies as the carbon efficiency. Total energy demand is closely linked to the energy demand for hydrogen production and the efficiency of hydrogen use. This can for example be seen in the results from Rosental et al. (2020) who report a total energy demand of 10.84 kWh/kg MeOH for point source capture and 13.09 kWh/kg MeOH for direct air capture.
It can be seen that although the energy demand for methanol synthesis of the microplant is low, its overall energy demand in the short term scenario is higher than other systems. In the medium term scenario, it is about average. Electrochemical processes tend to show a much higher total energy demand, with the exception of the system studied by Kalbani et al. (2016).
Based on the results in the LCI data table, it can be assumed that the favourable position of the microplant on the CC impact chart is the result of the low carbon intensity of the electricity supply modelled in this study. Still, the microplant is certainly not outperformed in a significant manner by its competitors.

8.7. *Cross-study – Discussion*

This chapter analysed published LCAs on CO_2-based and bio-based methanol production to enable a side-by-side comparison with the results of the LCA in this study. Here, some of the key findings are aggregated per topic as both a summation of this chapter and a collection of the main takeaways.

8.7.1. Key findings of CO_2-based r/f-methanol

Microplant impact similar compared to literature results, mainly due to the low impact electricity supply
Compared to reported Climate Change impact scores in literature, the microplant belongs to the best performing segment. Reported impact scores that were lower than those of the microplant (i.e. better) originated from studies that considered highly optimistic CO_2 feedstock sources (Artz et al., 2018), or that provided avoided burdens for co-produced products (Fernande-Dacosta et al., 2019). Key comprehensive LCA studies by Rosental et al. (2020) and Thonemann (2020) that include renewable electricity and infrastructure requirements showed comparable climate change impact scores. Explorative analysis showed that it is likely that the favourable position of the microplant is the result of the low carbon intensity of the modelled photovoltaic electricity. This is likely because in terms of key process parameters (i.e. feedstock use, energy demand), the microplant performs comparably or slightly worse than the systems reported in literature.

Heat and by-product integration as potential energy demand reduction pathways
Interestingly, multiple methods could be found that attempted to lower the total energy demand of the energy-intensive CO_2-based methanol production process and that thus might explain the lower energy demand compared to the microplant. More than once CO_2 was sourced from high purity chemical processes, thereby practically eliminating the large energy demand of CO_2 capture. This could be relevant for centralised CO_2-based methanol production due to the still large presence of high purity CO_2 sources in global chemical industries (Chen et al., 2019).

Other methods included the integration of methanol production in existing processes to make use of heat and by-product exchanges. This reduces the need for feedstock production and lowers the energy demand of the combined processes. Both these examples detail cases where centralised CO_2-based methanol production is closely linked to existing industries. In all fairness, this is not quite relevant for the microplant due to its probable application in more remote locations.

More applicable to the microplant is the frequent use of heat integration between key processes. About half the studies mention some form of heat integration, mostly between the exothermal methanol synthesis process and the energy demanding CO_2 capture or methanol distillation processes. In some rare cases, also heat integration of high-temperature alkaline electrolysis was found to be significant and beneficial (Rosental et al., 2020). A special case of heat integration was found in the work of Meunier et al. (2020) who valorised purge gasses by utilising heat from their combustion in other processes. Heat integration is not applied in the microplant version assessed in this study and could highlight a potential route for improvement that has been validated in literature.

Electrochemical conversion and synthesis: a potential future competitor

A newer technology that was also assessed in this literature review is the electrochemical conversion of CO_2 into methanol. Nabil et al. (2021) state that due to the characteristics of electrochemical conversion, it is more suitable to be used for storage of intermittent energy than its thermochemical counterparts. The reported electrochemical routes however, currently only exist at low technology readiness levels and show much higher energy requirements, making it less attractive on the short term. Still, taking into account its low TRL state, it might become a contender on the medium to long term.

Potential benefits of the microplant: Identifiable but not verifiable

Most collected papers did not offer enough depth to allow for a comparison on unique features of the microplant (e.g. used ready-made databases, offered little to no sensitivity analyses). However, a few general preliminary remarks can be made. For one, the DAC unit rather efficiently co-produces highly pure water for the production of hydrogen where other CO_2-based methanol projects have to produce this separately. One study (Biernacki et al., 2018) actually found this production of ultrapure water to be highly impactful, this could therefore be an area where the microplant has a clear advantage.

One of the main benefits of the microplant is its direct integration in an array of photovoltaic panels, allowing for autonomous methanol production in areas with high solar irradiation. This set-up reduces the need for additional electrical infrastructure that is normally associated with PV plants (e.g. inverts, grid connection). The combined autonomous operation and reduced material demand for the PV installation leads to the low impact electricity assessed in this study. Unfortunately this advantage could not be verified using the collected LCA works for a number of reasons that are briefly elaborated in 9.1.3.

Isolating insights remains challenging using the cross-study analysis approach

Overall, the side-by-side comparison proved its worth by enabling an initial validation of the environmental profile of the microplant and showing some potential improvements. Unfortunately the many sources of methodological and technological variation in the analysed studies prohibited more conclusive insights. For now, the most important insights are that from an environmental perspective 1) the microplant performs comparably to systems reported in literature, and 2) no reasons could be found for potential disadvantages of the microplant compared to standard process designs. Lastly, It is important to note that the cross-study analysis yielded no important parameters that were overlooked in this study. All of the major components that were discussed in the reviewed papers (e.g. major energy and material inputs, catalysts, process efficiencies) were also taken into account for the LCI and LCA of the microplant.

8.7.2. Insights of biomethanol

According to some author biomethanol routes are a viable contender for the production of low-carbon methanol. The cross-study analysis of biomethanol technologies is not included in this chapter and is instead elaborated in appendix H. In this section, only the main insights are briefly discussed to give .

Biomethanol shows a much wider range of impact scores compared to CO_2-based methanol
Biomethanol projects show greater variation in reported Climate Change impacts than CO_2-based methanol projects with some projects showing positive impact scores and some negative. Compared to the reported results of CO_2-based methanol, only one biomethanol system comes within the range of CO_2-based methanol systems that make use of renewable energy. This the case described by Fózer et al., (2021) who studied the dedicated cultivation of algae for methanol production.

Upstream emissions reduce many of the potential benefits of bio-based methanol
In the assessed works it was found that the carbon sequestration benefit of biomass is reduced due to methane emissions from agricultural practices and direct emissions from biomass conversion into clean and suitable syngas. The latter is a clear area where CO_2-based methanol seems to be superior due to the possibility circumvent the need for syngas production by directly hydrogenating the CO_2 feedstock with hydrogen. Biomass-based syngas furthermore is more prone to pollution and processes required to clean and condition the synthesis gas lead to harmful emissions that are relevant in climate change, toxicity and acidification categories. Internal transport of feedstocks also seems to be more significant for biomethanol and furthermore puts a strain on the overall CO_2-benefit of using biomass.
Biomethanol LCA studies reported much higher acidification, eutrophication, and photochemical ozone creation impacts in relation to conventional methanol than CO_2-based methanol studies in their comparison to conventional methanol. The heavy use of fertilisers to increase biomass growth appears to be the main culprit.

Assessed biomethanol studies were limited, and lower-impact systems can be envisioned
However, the analysed studies only describe a few potential biomass-based methanol systems and generally do not consider the use of renewable energy other than the combustion of biomass. If biomass treatment and conversion uses renewable energy, and if the biomass feedstock has not been acquired via fertiliser / herbicides / pesticides-heavy processes, a case can be made for bio-based methanol. This initial overview concludes that it is unlikely that biomethanol will outperform CO_2-based methanol in most impact categories, but impacts are highly case specific and actual comparison can only be performed on a case-by-case basis.

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9. Discussion

9.1. *The integrity of this LCA*

Before any recommendations can be made or conclusions can be drafted, it is necessary to reflect on the general integrity of the research performed in this study. In other words; whether or not the research questions can be answered in a satisfactory manner. This section discusses the limitations of both the research approach, and the execution of the research. The sub-chapter is divided in a section on the limitations arising from the goal & scope definition, limitations regarding the use of LCA in general, limitations regarding data collection & LCA modelling, and finally the limitations regarding uncertainty and the scenarios.

9.1.1. Limitations of the goal & scope definition

The goal and scope definition defines what is included in the research and what questions the research therefore can reasonably answer. It inevitably also *excludes* potential interesting areas that, after performing the research, turned out to be important to the overall understanding of the case study. The goal and scope definition in this study certainly limited some important questions that still surround the core topic.

Not all technological changes can be captured in the temporal scope

For one, the temporal scope of in this study is rather limited. This results in two distinct limitations regarding any conclusions that can arise from the research results. The microplant design itself, of course, is currently not realised on pilot scale. It merely exists in separate (functioning) proxy-setups in lab-setting. The amount of potential future developments is still very large and will increase with every step into the future. The current temporal scope merely covers the short term and medium term prospects of this technology, thereby roughly only considering the first pilot scale microplant and the microplant around market introduction. Many of the technological developments on the horizon are not covered in the short and medium term scenario. For example the inclusion of battery packs to increase microplant operation, the increase of the size of the microplant, or the use of different sorbents, are all not included in this study. This is in part due to the limited temporal scope and the lack of more forward looking analysis and exploration of potential future designs.
The second limitation of the temporal scope is that the reference system will not change significantly in the short-to-medium term, thereby perhaps painting an optimistic contrast between microplant-based-, and conventional methanol. Some major technological improvements can be expected for the production of methanol from fossil resources in the next 15 years, for example CO2 injection in the synthesis process or electrical heating (see chapter reference system, n.d.). Although it is unlikely that this would change the CC impact outcomes on a cradle-to-grave basis much, it could be important in the other impact categories.

The importance of the location of the methanol farm / PV plant is not captured in this study
The geographical scope is rather limited while this is actually relevant for the case at hand. The current microplant-farm is modelled with Oman as primary location. Sun irradiation is typically high in such locations, leading to a high power output of the photovoltaic panels. A methanol farm following the same concept might perform much worse in Europe than the location assessed in this study due to a lower irradiation and therefore a higher panel to microplant ratio. Additionally, the transport phase after the 'factory gate' is not considered while this could play a large role in choosing for nearer high solar irradiation locations such as Portugal. This lack of attention regarding the geographic coverage excludes a discussion on the location-specific benefits or adverse effects of the microplant.

Other potential local effects are the degradation of the sorbent, which is highly dependent on local conditions and at the same time is important for the performance of the microplant. Similarly, some of the impacts captured by certain impact categories are context-dependent. The emission of ammonia from the DAC unit could be problematic for fragile lush ecosystems that for example could be found in some of the more mountainous areas that have received attention as potential future locations for the microplant farm. The current study merely considers a single location; the desert like environment of Oman. The fixation on this particular location is most visibly reflected in the impacts of the photovoltaic system, which are arguably more favourable in this location than anywhere in Europe. The combined dependence of the microplant-farm on localized factors is large, and the results in this study merely study a single location. One should therefore be careful with extrapolating the conclusions to other locations that might show very different characteristics. Still, this is mitigated slightly by the interpretation sections on the role of electricity and the role of sorbent degradation. Both charts can help in gauging what the impacts of the microplant would be in different locations.

The case-based approach does not facilitate wider insights
Attributional LCAs are common practice because they offer answers to most questions and tend to not engage in complex modelling of cause-effect relationships. In this case however, one could wonder what the implications could be of large scale implementation of microplant-based methanol production. This research does not answer any questions of this magnitude as it fails to put the impacts into perspective. This is in part a result of the functional unit, which is 1 kilogram of Methanol at factory gate and not 'one megaton of methanol at the Port of Rotterdam'. Focusing on the factory gate as endpoint of the assessment disregards all potential effects of its larger scale implementation. Other papers such as the work by Ravikumar et al. (2020) do provide additional value to their research by including comparisons such as the direct use of renewable electricity for the grid coupled to conventional methanol production versus the use of renewable electricity for the production of co2-based r-methanol. Such assessment enables a discussion on the best use of resources from a higher perspective.

9.1.2. General critique towards LCA, and implications for this study

LCA does not measure all impacts
Life cycle assessment is not without its limitations, both with regards to the application of the method in general, and its application to the study of ex-ante systems.

An initial critique of LCA in general, is its low spatial and temporal resolution and the general lack of inclusion of social and economic aspects (de Haes, Heijungs, Suh & Huppes, 2004). The latter is not a major concern for this study as it is clearly stated in the goal and scope definition that social and economic aspects are not considered. The low spatial and temporal resolution however, is a limitation of LCA that hurts its ability to forecast potential environmental impacts. With the introduction of newer databases, such as the ecoinvent 3.7.1. database used in this study, the spatial accuracy has been increased. Databases now typically include datasets on country-level, and sometimes even on regional level.

Although databases have been improving, the calculation of local impacts still has ways to go. As has been addressed before, some potential damages that are aggregated into impact categories, are especially relevant on a local level. Another limitation to the used impact methods is that some impacts are not covered by the assessment. This is often due to a lack of knowledge about the cause-effect pathways of certain emissions (e.g. novel entities: Curran, 2014) or because the debate on how to approximate certain impacts is still ongoing (e.g. material scarcity: Vogtländer, Peck & Kurowicka, 2019). For the case of the microplant LCA, this limitation reduces the suitability of the study to assess the material demand, which is higher than conventionally produced methanol.

LCA models merely offer a simplified reflection of reality
LCA models furthermore attempt to describe a complex world from a holistic perspective in order to better understand implications of human activity. In order to make this task manageable LCAs simplify real world situations and limit the area of study to what is deemed acceptable to the LCA practitioner. Of course if an LCA practitioner would be to continuously expand the studied system it would eventually encompass the entire world (as explained by von der Assen et al., 2014). Certain decisions therefore need to be made about what to include and what to exclude from the system boundaries. In this study, that for example led to the exclusion of manufacturing processes (e.g. injection moulding) from the product system. This naturally removes the possibility to confirm the hypothesis that manufacturing processes are not relevant at this scale.
Additionally, LCA models typically are linear steady-state models of physical flows (Guinée et al., 2002). This (over)simplifies all sorts of processes that have a dynamic nature. The microplant for example, only runs when a certain illumination threshold (translated in produced PV power) is reached. In a certain order, the sub-systems then receive power and start operating. This process is far from static and could be highly dependent on local conditions.
LCA is not well-equipped to deal with dynamic models, which is why often software packages such as Aspen Plus or detailed PV modelling software are used that are better suited for this job. This has not been done in this study however, which potentially overlooked unexpected efficiency improvements or reductions as result of process dynamics.

9.1.3. System boundaries and carbon accounting

The cradle-to-gate perspective is prone to misinterpretation but can be justified
A cradle-to-gate perspective forgoes addressing the perhaps critical use phase of renewable methanol Guidelines on LCAs of CCU generally (strongly) discourage the use of system boundaries that end at the gate because in many CCU cases CO_2-based products actually provide a different service than their conventional counterparts, not including this different use then could lead to wrong conclusions. The duration of the storage of carbon dioxide and its emission medium can furthermore be important in the calculation of the global warming potential (von der Assen, 2014) though other authors contest this (Müller et al., 2020). In addition, carbon neutrality or negativity should only be claimed if the full lifecycle is considered, which was conveniently omitted by many past publications (Tanzer & Ramirez, 2018).

In this study the argument is made that the methanol produced by the microplant really does provide exactly the same function as conventionally produced methanol. As von der Assen et al. (2014) explain: "*If methanol quality and suitability for the different uses is the same for all methanol production technologies, the downstream processes of methanol utilization can be omitted in LCA. This simplification to the cradle-to-gate scope is very convenient for commodity producers who do not even know in which way their commodity will be used after sale."*
In conclusion, the production of methanol using Direct Air Capture is perhaps the most convenient case study considering all challenges that are normally faced by LCAs of CCU-products, this is entirely due to the fact that methanol is a basic chemical and that Direct Air Capture captures CO_2 without needing to address the potential emitting sources of CO_2.

As argued by Ramírez Ramírez et al., (2019) and Müller et al., (2020), the proper accounting of carbon dioxide and the setting of correct system boundaries is crucial for the LCA of CCU products. An often made assumption in these kinds of LCAs is the omitting of the CO_2 capture processes under the assumption that high purity co2 is freely available from industrial processes. However, as von der Assen et al. (2013) explain; feedstock CO2 can never have a global warming potential of -1.0 kg co2 eq. / kg co2. Carbon dioxide is furthermore not included in any LCI database, so it cannot be used in LCA whilst assuming that its upstream chain is accounted for. To the best of knowledge, this study addresses this challenge by fully including the capture system within the system boundaries. The feedstock co2 that enters the compression system in this study already carries with it the burdens of the direct air capture process of around -0.91 to -0.88 kg Co2 eq.

9.1.4. The inventory of this LCA

The issue of single-source data collection for emerging technologies

Most of the process data that populates the unit process data and the scenario parameters in this study, were received directly from the technology developers. At the onset of this project, the technology developers shared an excel sheet detailing the most important energy/mass flows and a parts list. This file was based partially on lab-scale results but mostly on expectations from previous research projects at ZEF BV. The file therefore already stood for a certain assumption about the future performance of the microplant, as it has not been fully tested in a single design as of yet. The uncertainty and variability that inevitably stems from this approach to unit process data generation, has been further explored in the interviews for the ex-ante scenarios. The mass balances were furthermore subjected to a total mass-balance, which considered the total amounts of carbon, hydrogen, and oxygen input in the system compared to their total output. With some iterative small adjustments, the overarching file was deemed suitable for the LCA model. After the compilation of the scenarios, the initial excel sheet most closely mimicked the short term neutral scenario.

One can wonder whether the technology developers are impartial in this project. For that reason, most data was cross-checked with values reported in literature. For the DAC unit for example, the energy use was compared to the work by Deutz & Bardow (2021), for the AEC unit the work by Delpierre et al. (2020) was consulted. The cross-study analysis, especially the LCI comparison, furthermore allowed for additional comparison. From the combined comparison, there have not been any incidences where initial values could be seen as too optimistic. Optimistic assumptions about technology development is consistently addressed in the scenarios, and transparently communicated.

Still, the before the results in this study are copied or considered in other contexts, it would be desirable to have an external expert review the unit process data of all major processes.

The need for proxy data and potential results

Regarding the hierarchy of LCI from Parvatker & Eckelman (2019) the use of proxies was avoided as much as possible and has only been applied for the approximation of the stack actuator in the alkaline electrolysis cell and for a single feedstock chemical for the production of the sorbent. The latter was done with a chemical that is nearly identical to the required chemical. The use of a proxy for the actuator however, turned out to be more impactful in all impact categories than was initially expected. Still, it was chosen to keep this proxy in the model as a to also account for the material demand of electronics, and their respective impacts. This will receive more attention in the recommendation section of the discussion.

9.1.5. Modelling approach

Unit processes as opposed to the black-box approach

In the LCA model in this study the standard modelling approach was used where rough process data is divided into individual unit processes and normalised so that all environmental and economical flows align with the production of one 'unit' of the process' main product. The benefit of this approach is easier scaling of upstream processes to match the demand by downstream processes. It furthermore provides an easier to understand database.

The model using 'normalised' unit process data in this study was compared to the model using non-aggregated unit process data (i.e. not scaled to match one unit of product output from each process). A small difference (1-2%) in impact results could be identified, which is probably the result of the aforementioned matching of upstream and downstream processes. Still, it could not be confirmed whether this is actually the case and the exercise identified a potential inconsistency in the model.

To adhere to the standard, the normalised unit process approach was used for the result collection process.

Recycling in LCA can significantly influence LCA results and only one approach has been followed

The modelling of recycling in LCA can be done following multiple underlying philosophies, this study opts for the cut-off approach. Under the cut-off/recycled content approach the share of recycled material in the initial material input in production processes should be modelled. The problem with this approach is that the upstream supply chain of, for example, recycled silicon is not yet included in the most recent ecoinvent database. It is then an additional strain on the LCI phase to collect relevant data and adapt background processes. Another option would be to opt for the avoided burden approach which takes into account the reduction of impacts of new production that uses secondary material from the former product system. Similar issues of data availability and the necessity for assumptions are relevant under this approach as well. However, Frischknecht (2010) argues that in view of wider value judgements regarding environmental sustainability, the avoided burden approach assumes a 'weak' sustainability point of view (Neumayer, 2003; as cited by Frischknecht, 2010). The idea being that only the cut-off approach considers the impacts at the time they occur whereas the avoided burden approach considers the potential and highly uncertain future of end-of-life material recovery. In strongly circular product systems (i.e. new beverage containers) the avoided burden approach may be useful but it can be argued that the approach does not suffice for product systems with poor circular performance. In addition, considering the lifetime of 30 years for e.g. a PV system combined with the avoided burden approach would mean that the LCA results underestimate the impacts for the duration of the lifetime and until the material is recovered. The large challenges regarding sustainability and resource use that we face today do not allow us to rely on potentially avoided burdens far into the future.

The implication of the above for the LCA model can be very significant, as no avoided burdens are provided to the microplant for the recovery of materials at the end-of-life. Compared to studies that might provide those avoided burdens, the microplant would have a disadvantage in most impact categories. The modelling choices underlying the cut-off approach are detailed in the appendix L. The issue of recycling in LCA remains a subjective choice for the LCA practitioner. In this case, the argument is made for the cut-off approach, but other approaches should be considered as validation if material demand is a primary concern.

LCA software sometimes caused errors with parameterised datasets
All required calculations for the LCA are performed using the Activity Browser, a graphical add-on to the open source Brighway2 python package. For the duration of this project, this software showcased some inconsistencies with calculating the results from a strongly parameterised dataset. There were instances where functions in imported databases were not actually calculated unless they were manually re-added. Besides frustration, the difficulty of identifying such errors could have rendered some errors to remain in the model. The frequent exporting and importing of foreground datasets into the AB has probably mitigated most of the effect stemming from such errors. However, unless the model is re-made in other LCA software the influence of the quirks of the AB on the LCA results are difficult to estimate.

9.1.6. Uncertainty and scenarios

"(the best) remedy for deep uncertainty is to think about the future in terms of multiple plausible outcomes rather than probability distributions". Maier et al. (2016) (as cited by van der Giesen et al. 2020)

How likely is it that the scenarios offer a true reflection of the microplant in its future state?
This question again links closely to the goal and scope definition of this research project. The most important goal is to guide technological development with an understanding of potential environmental implications of changes in the design. In itself, this goal does not impose the requirement to capture the actual future state of the technology in the scenarios, it merely requires the model to show how design variations might influence the environmental profile. In the formulation of the other research questions however, more precision can be demanded.

Some technological developments are left out but scenarios include the most likely parameters
As addressed briefly before, the scenarios consider variance in the energy demand of individual subsystems, the use of material, the consumption rate of consumables, and the impacts of energy generation. Besides some assumptions that lie at the foundation of the scenarios (i.e. autothermal MSR, limited heat integration) the scenarios do not consider major changes in the design the microplant, and major changes in its modes of operation. A few probable future technological improvements are for example the recycling of water from the distillation column to the alkaline electrolysis unit to limit the energy demand of the DAC unit, the increase of the size of the microplant for a variety of potential benefits, and the addition of battery packs to the microplants that can be charged during the day and discharged during the night to continue the production of methanol. Naturally, such developments would have a large impact on the environmental profile. The mentioned examples however, are still highly uncertain at the moment of writing and there is yet no consensus about whether or not these improvements will actually occur. The scenarios in this study on the other hand, encompass those parameters and improvements that (with greater certainty) are likely to change over the next years if

development continues at the current rate. The scenarios furthermore do so consistently, meaning that the underlying assumptions have been discussed and studied before using them in the calculation of the model.

It cannot be concluded with great certainty that the scenarios actually describe the future state of the microplant in approximately five and ten years. The current study describes the potential future of the microplant using its current design as vantage point and extrapolates various developments that do not wander far from the design. If major changes are not implemented, the results of this study will hold its value. If, on the other hand, certain adaptations to the design are made that are not reflected in the scenarios in this study, new studies should be periodically performed to safeguard the sustainability of the technology. For such further studies, this work can be the foundation.

Scenario-caused impact variance might be overshadowed by project-level uncertainty

In some categories such as Climate Change the scenarios only introduce a small variability in impact scores. Like any ex-ante assessment, this project is faced with great uncertainties due to the lack of experimental pilot-scale data, the extended need for assumptions, the lacking ability to verify original data provided by ZEF, and the general ‘unknown unknowns’ that come with future predictions (see the literature review of ex-ante LCAs). In some categories the combined effect of such uncertainties likely outweigh the significance of the scenarios, reducing the overall usefulness of the scenario-approach to capture such uncertainties in impact ranges. The direct effect is that actual impacts may lie beyond the range projected by the scenarios, hampering the ability of this study in answering the research questions and meeting the research goal.

Considering this potential effect, it might have been better to adopt a more extreme perspective during the drafting of the scenarios, i.e. using very pessimistic assumptions instead of a pessimistic viewpoint with some neutral notes. The results set forth in this study are still relevant, but the reader is advised to consider the possibility that uncertainties may cause impacts outside of the introduced ranges.

9.1.7. The cross study analysis

The lack of consistency between CO_2-based LCAs makes it difficult to build on previous work
As a general remark on the state of CCU-methanol LCAs in academic literature it should be noted that the many sources of variation are problematic for these assessment of technological pathways by other actors. In this study, both the lacking sample size and the many origins of variation between studies hampered further analysis. Because of this the importance of choices regarding methodology and the technological processes could not be fully assessed. This compromised the overall ability to reach deeper conclusions on the performance of the technology assessed in this study in relation to its competitors as reported in relevant literature. This has consequences both for the quality of this study and future technology developers such as Z.E.F. B.V. who have the desire to preliminarily estimate the environmental performance of the technologies developed in their care.

Cross study analysis is a dubious method for providing more profound insights
The cross study analysis exercise of this research project and the subsequent difficulties of answering the research questions using this method, proved that to reach deeper insights a full modelling of multiple alternatives in the foreground system is required. The modelling of alternatives allows the researcher to more conveniently compare critical areas between assessed technologies. While the initial modelling stage might put an additional strain on the study's resources, it will likely save time in the interpretation phase. Unfortunately this piece of wisdom comes too late for this research project, it is hoped that future projects might benefit from the lessons learnt.

9.1.8. Research integrity and research objectives

The integrity of this study is challenged by a couple of key limitations;

1. The impossibility inherent to ex-ante LCA to capture all technological future developments of the microplant and the lacking geographical scope. This limits the usefulness of the assessment to the point where the design of the microplant is changed significantly.
2. The limitation of Life Cycle Assessment to include all impacts. This might underestimate certain impacts, especially those of material demand and those that are relevant on a local level.
3. The limited reliability of data. Data has been collected with the help of experts and validated with literature but validation was only brief and potential optimistic data can influence the impact results.
4. The LCA modelling software has shown errors, though considerable effort has been put into identifying and improving these errors, it cannot be guaranteed that the actual model is completely free of errors.
5. The cross-study analysis was found to only be able to answer the research question to a limited extend, leaving potential valuable insights to be only discoverable through comparative life cycle analysis.

With the available resources in this project, it was attempted to mitigate each of these limitations as well as possible through the process of iteration that is key to life cycle assessment. Because tools to quantify the result of the limitations are lacking, it remains difficult to estimate the effect of the limitations on the integrity of the results. However, considering the aforementioned iterative process with frequent supervision of case-experts, it is expected that the outlines of the result can be used to draft a first set of conclusions regarding the environmental performance of the microplant.

9.2. *Recommendations in discussion*

Whether or not action should be undertaken based on the results from the Life Cycle Assessment can be difficult to assess. LCA studies therefore sometimes include a process of normalisation, which attempts to communicate the relative significance of the category indicator results (Guinée et al., 2002). It does so by normalising the indicator results relative to reference information, often on a regional level. An additional weighing step can then involve the value choices of important stakeholders in order to further aggregate impacts and enable better comparison between alternatives. Yet, normalisation and weighing still communicates the severity of impacts based on a reference case, which leaves the question how much we actually know about the reference case and its desirability. To solve the extended issue of a reference case, some LCA practitioners expand the reference case to encompass the absolute boundaries of our planet. These so-called planetary boundaries (PB), introduced by Rockström et al. (2009), detail a number of key planetary processes with assigned thresholds that together define a safe operating space for (human) life on earth. Consalez-Garay et al. (2019) for example, based their impact assessment of low-carbon methanol on these planetary boundaries, thereby providing more perspective for the actual value assessment of the impact indicator results. The inclusion of planetary boundaries is not widely applied in LCA, rigid methodology for it is still lacking and including it here is much beyond the scope of this study. Regardless, the planetary boundaries will be briefly considered in the discussion as a means to determine whether differences between the microplant-approach and conventional methanol production are important and should deserve further action or research. If, for example, the microplant performs worse than conventional production in a category related to a planetary process that is past its safe threshold, measures should be undertaken to mitigate these impacts. The technological part of the discussion is further structured via a set of questions that have arisen from the impact results and the interpretation. The following questions will each receive a brief section:

1. Should flaring be applied in the microplant system?
2. Should the emissions of the DAC system be mitigated?
3. Should the material demand of the microplant receive more attention?
4. Should the PV panels be produced in Europe instead of China?
5. Is the continuous increase of energy efficiency the most important parameter?
6. Micro vs. Macro; How would the microplant fare against macro-scale CO_2-based methanol?

9.2.1. Should flaring be applied in the microplant system?

Purged gasses and their characterization factors

As a recap, direct emissions from the methanol reactor occur on a small scale to measure the composition of the reactor contents and on a larger scale to purge the reactor from accumulated nitrogen. Some of the gasses are coupled to characterisation factor. In impact assessment methods (i.e. ILCD 2018) that means that previous research has indicated that release of the substance to environmental compartments (i.e. water, air) is related to adverse effects on climate change, ecosystem quality, or human health. The most relevant emissions from the reactor are carbon dioxide and hydrogen, the two feed-gasses which constitute most of the feed-flow that is occasionally purged to rid the reactor of nitrogen. Methanol and carbon monoxide are emitted in smaller (trace) amounts. Under the ILCD 2018 impact method, methanol has a characterization factor for freshwater ecotoxicity, non-carcinogenic effects, and photochemical ozone creation. Carbon dioxide and carbon monoxide of course attribute to the Climate change category but carbon monoxide also to the photochemical ozone creation category, albeit far less than methanol (4.6E-2 vs 23.6E-2 kg NMVOC eq.). Hydrogen is not coupled to any characterisation factor in any of the impact methods.

Larger methanol emissions could introduce new trade-offs, though emissions only occur in trace amounts

Considering the above, the purging of feed-gasses will not have much of an effect in any impact category. The incidental emissions of methanol from the 'measure outlet' however, might be problematic due to its high ozone creation potential. Indeed, the emission of around 4.8 grams of methanol per kg of methanol produced, increases the photochemical ozone creation impact score with 234%, thereby also becoming more impactful than conventionally produced methanol by roughly the same factor.
Potentially, the this can have important consequences. Via two cause-effect pathways the formation of ozone impacts human health and terrestrial ecosystems (LC-Impact, n.d.), it furthermore is best linked to the 'atmospheric aerosol loading' planetary boundary. Unfortunately, this particular planetary boundary remains one of the most elusive due to scientific uncertainty in this field (Duvic-Poali & Webster, 2021). Regardless, a photochemical ozone creation indicator score that is over two times as high as conventionally produced methanol might indicate a problematic trade-off.

A global warming potential for H_2 could reduce the climate change benefit of CO_2-based methanol

Additionally, there is the issue of impacts resulting from the emission of hydrogen. Clearly, the potential impacts of hydrogen in the atmosphere are still debated, as none of the include impact methods contains a characterization factor for hydrogen. Still, some papers indicate that hydrogen might function as an indirect greenhouse gas (GHG) by reacting with hydroxyl radicals (Derwent et al., 2020). Hydroxyl radicals are an oxidizing agent in the troposphere and their reduction contributes to an extended lifetime of GHGs such as methane. Consequently, hydrogen emissions also indirectly influence ozone concentrations, potentially adding to the depletion of the ozone layer in the stratosphere. The influence of hydrogen emissions in the ozone depletion category are not likely to be relevant, as this is one of the categories where the impact of conventionally produced methanol is far greater. The global warming potential however, might be more relevant to the microplant's environmental profile and its position in relation to other low-carbon methanol production pathways. Derwent and colleagues estimate that the global warming potential of hydrogen lies around 5 (+- 1) kg CO_2 eq. over a 100-year time period (Derwent et al., 2020). Significant emissions of hydrogen in the methanol production chain might therefore partially mitigate the beneficial effect of CO_2-based methanol.

More research necessary to quantify the GWP of H_2, the option to add flaring later should be considered

The concerns of hydrogen emissions are most often voiced in papers discussing the wider implications of the hydrogen economy, thereby assessing the potential adverse effects of hydrogen emissions on a very large scale. Hydrogen emissions on the level of the microplant might not be important, especially considering the volatile, dissipative, and short-lived nature of hydrogen in the atmosphere. Given the current state of the scientific field in this area, it would be to soon to impose measures merely on the bases of hydrogen emissions alone.

Before the main question of this section is answered, it should be assessed if it is realistic to assume that these emissions would actually take place in a future microplant-context. In an additional talk with the technology developers, it was found very unlikely that methanol, in the amounts discussed here, would actually be expelled

via the purge exit. The main argument is that methanol condensates within the system and is therefore not easily purged together with the other reactor contents. Actual methanol emissions would likely be in trace-amounts.
Taking this into account, it is not by definition recommended to design a flaring system for the microplant. It would be however be wise to periodically consult the state of knowledge regarding the global warming potential of hydrogen. To be able to anticipate any such updates, maintaining the option to add flaring later should be considered in the design of the microplant.

9.2.2. Should the emissions of the DAC unit be mitigated?

DAC emissions and its characterisation factors
The life cycle inventory explained how degradation of the sorbent can lead to emissions of degradation compounds from the DAC sub-system. In the interpretation chapter the underlying assumptions were investigated which showed that amine emission are highly dependent on the sorbent lifetime (i.e. degradation rate) and the assumed conversion rate of degraded sorbent into ammonia emissions. Taking the same approach as the previous section, one can see that the ILCD impact method contains characterization factors for ammonia in the freshwater & terrestrial acidification, marine eutrophication, terrestrial eutrophication, and respiratory effects impact categories. On a microplant level (excluding electricity impacts) the emissions from the DAC unit are relevant in all categories, with 18%, 5%, 43%, and 24% respectively.

Damage effect pathways of ammonia emissions
The eutrophication categories align with the biochemical flows planetary boundary, which according to the authors, is stretched far beyond a critical threshold (Steffen et al., 2015). The currently problematic state of the biochemical flows planetary boundary is mostly the result of human agricultural activity due to the production and use of fertilizers but other emitting sources can still be relevant. Terrestrial acidification can be linked to the PBs of ocean acidification and biosphere integrity due to the impact that acidification can have on both aquatic life and vegetation. Especially the biosphere integrity is considered to be at a dangerous threshold. The respiratory effects impact category is not as easily linked to a planetary boundary, regardless, as mentioned in the section on sorbent emissions, ammonia can be damaging to human respiratory tracts. Combined, from a planetary perspective, the emission of ammonia could be thus be rather important.

Intuitive comparison: agriculture vs. DAC emissions
To provide a non-scientific estimation about the severity of ammonia emissions, the potential ammonia emissions are compared to the average emissions per hectare of utilised agricultural area in a back-of-the-envelope calculation. Assuming the yearly average emission of 20.3 kg NH_3/ha of agricultural land (Murawska & Prus, 2021), and an average agricultural business stretching 16.6 ha (Eurostat, 2018; larger farm), this comes to a yearly emission of roughly 337 kilos of ammonia per agricultural business in the European Union. To estimate the yearly DAC emissions of a microplant farm, two scenarios are composed using the graph from the interpretation chapter. The first is slightly pessimistic, assuming a sorbent lifetime of 2 years (replacement at 20% degradation) and assuming that 20% of the degraded compounds is converted into ammonia emissions. The second scenario is slightly optimistic, assuming a sorbent lifetime of 4 years and only 10% emission of ammonia. A microplant farm consisting of 3500 units then yearly emits 175 kg of ammonia in the pessimistic scenario and 43.75 kg of ammonia in the optimistic scenario. This is a wide range but it does help in intuitively understanding the significance of potential impacts resulting from DAC operation. Merely from the comparison with an agricultural business and the current state of the biochemical flows PB, it would be advisable to undertake action to counteract the emissions.

The uncertainty of both DAC emissions, their local impacts, and subsequent recommendations
A potential mitigating factor for the severity of ammonia emissions that has been introduced already in this study is the regional aspect of some of the impact categories. Characterization factors included in LCIA often do not consider local sensitivities of biomes in the case of ecosystem quality, and the presence of populated areas in the case of human health (with exception of the 'urban-air' emission compartment). There is a fair point to be made about whether ammonia emitted in an arid environment such as Oman is as damaging as in a lush environment, as is for example the case for the aforementioned agricultural businesses. Again, regarding the severity of the potential impacts, it is necessary to gauge if it is likely that the inventory and LCA model in this

study accurately represents the system in practice.
Unfortunately, the analysis of amine emissions in this study is severely hampered by both the lack of knowledge about emissions of sorbent degradation and the issue of missing characterization factors. There is for example no characterisation factor for the potential evaporation of the sorbent in its entirety (i.e. whole molecule), neither were potential emissions included other than ammonia. Although it is likely that ammonia is the most relevant emission, it is also possible that other compounds are emitted that each have their own adverse environmental impacts.

Combining the uncertainty about DAC emissions with the issue of lacking localised characterisation factors, it is difficult to provide a definitive answer on the issue of DAC emission mitigation. The technology developers are generally advised to consider the potential impacts of amine-related emissions with regards to the local context. Depending on a more context-specific assessment, additional systems can be added to the DAC unit that almost entirely eliminate its emissions. Technologies that do so are readily available and for example include water wash systems are already implemented to prevent emissions from MEA-based post combustion capture systems (SEPA, 2015).

9.2.3. Should the material demand of the microplant receive more attention?

Micro vs. macro energy technologies
The microplant approach to methanol production stands for a relatively new approach of decentralised energy carrier production that consists of mass-producible units, thereby omitting part of the start-up costs of larger plants and benefitting from the economies of scale of large scale manufacturing. Similar trends can be observed for energy storage in non-lithium batteries and for the production of hydrogen. A perhaps easy to follow hypothesis is that decentralisation of energy storage and energy carrier production could lead to a higher total material demand, as each individual unit is supposed to run independently, containing all necessary systems for production and relying on its own control systems. On the other side is centralised production where systems/process units typically contain much larger volumes and an overarching control system.

In this study it has been shown that the microplant approach to methanol production is coupled to a significantly larger minerals and metals depletion potential compared to conventional methanol production. International bodies such as the IEA closely monitor the global demand for metals and minerals and warn for possible scarcity with regards to the high demand for metals and minerals as result of the impeding transition towards cleaner energy technologies (IEA, 2021). The higher material demand of the microplant can therefore have an influence on the overall value judgement of the microplant concept and the conclusion about its environmental profile. There are however, two main factors that prohibit the exploration of this topic.

The impact of material use in LCAs is controversial
Firstly, the appropriation of scarcity (or material use in light of global rising demand) in LCA has been part of an ongoing academic debate that so far has not resulted into the 'institutional' integration of scarcity indicators (Vogtländer, Peck & Kurowicka, 2019). Conventionally, LCA considers material use in terms of absolute depletion, thereby merely assigning an equivalent factor of the depletion of a reference material. This disregards short-term supply risks which characterise the now rather famous term 'critical raw materials' (CRM) which is also used by the IEA and European Union to describe impeding conflicts arising from the need for energy-related materials. Many researchers have attempted to make critical raw materials workable in LCA, for example by implementing statistical risk factors (VAR; by Vogtländer et al., 2019) or by compiling characterisation factors on the basis of material concentrations in the Earth's crust (Arvidsson et al., 2020). Databases with characterisation factors are available and could lead to more wisdom regarding the relation between this topic and the microplant. Yet, the inclusion of such characterisation factors would require additional scrutiny in the form of an extensive literature review, uncertainty analysis, and added discussion, each of which fall outside of the direct scope of this study.

Implications of material estimations within this study
The second issue with properly addressing the material issue is that the material input for infrastructure and capital equipment is perhaps the most uncertain factor of the life cycle inventory. The use of a proxy to represent the actuator for the AEC unit for example, is relevant over most impact categories and especially the

minerals and metals category. The same counts for the estimated wiring needs and the demand for printed wiring boards and logic processors in the overall embodiment of the microplant. This uncertainty is further aggravated by the fact that the databases that make up these components can be dated back to 2007 and might therefore significantly overestimate their material use.

As a consequence of the above, this study is not well-equipped to answer the question of whether the material demand of the microplant should receive more attention. And on a broader scale, whether a centralised or decentralised approach to CO_2-based methanol production is most desirable. The impact results however, do provide a contrast for the material use between conventional production, and production via the microplant concept. Consistent efforts to reduce the total material demand of the microplant can therefore be expected to represent a clear technological improvement pathway.

Recommendation: continued attention for material use in further development

To make the case for the microplant approach to CO_2-based methanol production, the technology developers are advised to consider the overall demand for CRMs and other minerals and metals. This includes taking into consideration the idea that the decentralised approach inherently puts a larger strain on global resources than centralised production. Essentially, any increase or decrease in material demand is magnified a thousandfold in a microplant-farm setting.

As mentioned before, it falls outside of this study to assign specific targets to material use. However, replacement of certain materials or clever purchasing at certain manufacturers might significantly reduce the role microplant-based methanol in a global resource crisis. Copper for internal wiring could for example be replaced by aluminium or parts could be purchased from manufacturers that concern themselves with material scarcity.

In addition, specific improvements that are already known by the technology developers, are the reduction of nickel in the AEC unit by optimising its operating parameters or opting for more high-tech electrodes. Catalyst use in the methanol reactor on the other hand, does not arise from the assessment as a significant area for improvement.

9.2.4. The role of electricity: Should the photovoltaic plant be sourced from manufacturers in Europe?

A literature check of the low impact electricity in this study

The relevance of impacts related to PV electricity generation spans across all categories. In some categories it even dominates the overall impacts.

Arguably, this study considers a rather favourable PV upstream chain, leading to an overall low carbon intensity of the electricity supply. Although it cannot be confirmed without an extensive comparative analysis, it is likely that the low carbon intensity of the electricity supply is the result of positive expectations of the PV technology as introduced in the ITRPV report. The report mentions that before 2020, major process improvements temporarily stagnated and that from 2021 onward, major improvements can be expected (ITRPV, 2020). This is for example reflected in the generally reduced energy demand for most key processes of PV production, such as ingot pulling, wafering, cell production, and panel production. The contrast between the impact profile of photovoltaic electricity in this study and the profile from PV electricity in ecoinvent is large. The difference with the most up to date Life Cycle Assessments on silicon PV modules however, is much smaller (Müller et al., 2021). Müller and colleagues reassessed the inventory of photovoltaic panels using updated interviews and workshops with PV manufacturers and experts. They found that the average carbon intensity of produced electricity lies somewhere between 13-30 grams of CO_2 per kWh, as opposed to just below 11 grams of CO_2 per kWh in this study (2021-2025 scenario). The authors furthermore assessed panels under average European solar irradiation of 1391 kWh/(m^2 yr), and using the best to-date available data from before 2021. The assessment in this study considers solar irradiation in a dessert location of around 2400 kWh/(m^2 yr), and includes expected process improvements up until 2030. These underlying assumptions are likely to be the source of variation between the mentioned carbon intensities.

Realistic recommendations for PV impact mitigation

Because of the relevance of PV electricity for all impact categories, any impact reductions in the upstream chain will therefore benefit the environmental profile of the microplant-methanol in each category. Like any other CO_2-based methanol project using hydrogen from electrolysis, the changing the source of electricity is thus the single most impactful tool to tweak the environmental profile of the produced methanol. At the same time, electricity generation is often outsourced and undertaking action to mitigate its impacts does not always fall inside the sphere of influence of the developers. For that reason, the recommendations regarding this topic are not directed at detailed technological improvements but rather at what the technology developers could actually do.

As shown in the interpretation chapter, merely the replacing the Chinese heat and electricity processes with European ones reduces the CC impacts with 20.0% in 2025, and 18.6% in 2030. These benefits are shown in all other categories, with the exception of freshwater eutrophication and ionising radiation categories due to the larger presence of nuclear energy in the future European electricity mix compared to the Chinese electricity mix. Similar benefits of moving manufacturing from China to Europe were found by Müller et al. (2021) with additional larger benefits in the eutrophication (Marine & terrestrial), acidification, particulate matter, and photochemical ozone creation categories. These include some of the categories that are in a problematic range for the competitiveness of the microplant as compared to conventional methanol production. It therefore seems a rather promising option to opt for European manufacturers.

In addition, due to the relevance of panel design in the overall impact profile, the developers could look for manufacturers offering frameless panel designs or manufacturers who make use of low-impact encapsulation sheets, both of which are new trends in the PV market and could reduce material-related impacts (ITRPV, 2021).

Recommendation check: Advances in European PV manufacturing

One can wonder whether it is in fact possible for the technology developers to choose European PV manufacturers, as PV manufacturing in Europe has been known to lack behind in the global market (Frauhenhofer ISE, 2020). Prices of panels produced in Europe are typically greater and less competitive compared to panels produced in China. However, in the recent years the European Union, together with major players in the PV market, has deployed large scale investments to increase the competitiveness of the European PV market. The Highlite2020 project for example, sets out to research environmentally- and cost-competitive high performance PV technology with a focus on its practical realisation (Highlite, 2021). Considering these recent developments, it could be likely to assume cost-competitive production of photovoltaic panels in Europe. The technology developers are advised to keep track of these developments, as opting for European manufacturing could quite drastically reduce the impacts of methanol produced by their microplants.

9.2.5. The role of gradual efficiency improvements

The need to improve energy demand from an environmental and competitive perspective

Besides sourcing the PV panels elsewhere, an obvious improvement would be to reduce the overall energy demand from the microplant. As could be seen in the comparative LCI overview of the cross-study analysis chapter, the total energy demand of the microplant is higher than the average energy demand for CO_2-based methanol in the short term scenario, and about average on the medium term scenario. Considering the comments of the technology developers about the (perhaps rather optimistic) probability of the medium term optimistic scenario, the overall energy performance of the microplant is slightly below average compared to reported LCIs in literature. Should the overall performance of the microplant with regard to energy use thus be improved?

First of all, the energy demand of CO_2-based methanol reported in literature is often based on modelling software which might categorically underestimate the added energy demand that comes with the dynamic modelling of manufacturing processes. An example is the Operational Equipment Efficiency, which details the overall uptime of the processes in relation to its downtime. The decentralised approach to microplant-based methanol probably is probably less impacted by downtime because even if a couple of microplants suffer from a malfunction, thousands of others will continue production. In addition, the intermittent nature of renewable electricity and the consequences of this intermittency on downtime and start-up times for centralised CO_2-based methanol projects was almost never discussed in the assessed LCAs. It can therefore be argued that other reported energy efficiencies might underestimate the total demand.

Energy improvements as part of already ongoing research within ZEF

Of course, the overall energy demand remains an important key performance indicator. At risk of stating the obvious, improvements in the compression system (FM), methanol synthesis reactor (MS) and distillation unit (DS) are not very relevant on the microplant-level. Small improvements in the direct air capture unit and especially the alkaline electrolysis cell are much more closely linked to beneficial returns in the overall environmental profile. Still, some large expected improvements in the compression system (e.g. much more efficient compressors), and the methanol reactor (e.g. fully autothermal) could already move the total energy demand of the microplant into a competitive range with results reported in literature.

As explained in the life cycle inventory chapter, the energy demand of the AEC is not primarily a matter of general technological development but one of CAPEX/OPEX considerations. This is less the case for the DAC unit which shows clear pathways towards a more efficient energy use. One of these pathways is the application of heat integration between the at high temperature operating AEC and the heat-requiring DAC. This type of energy optimisation could often be found in the CO_2-based methanol LCAs, which considered heat integration between the methanol reactor and the distillation system or the CO_2-capture system.

Because the energy demand of the microplant is already subject of extensive research efforts by the technology developers, there are no additional recommendations regarding this topic.

9.2.6. Micro vs. Macro for CO_2-based methanol projects

To put it bluntly, this research project is not equipped to engage in a deep and conclusive analysis of the benefits and pitfalls of the microplant approach towards CO2-based methanol versus regularly sized ‘macro’-plant CO2-based methanol production. It does however, contain some preliminary insights that allow an initial discussion on the micro vs. macro approach as a starting ground for further research.

The integration with photovoltaic electricity

ZEF argues that the integration of microplants directly with photovoltaic panels provides a number of benefits that may be visible in the environmental profile. The first argument is that the direct integration reduces the need for wiring between PV panels and between panel arrays and the factory, while the same integration also eliminates the need for inverters to change the panel output from DC to AC. The second argument revolves around the assumption that centralised factories have longer start-up times and cannot make use of intermittent energy from PV panels with the same efficiency as the microplants. This would result in the need for backup energy, which would likely be via a connection to the grid, leading to higher energy-related impacts. Although the exclusion of inverters was considered in this study and led to lower PV related impacts, the second point cannot be verified. None of the assessed CO2-based methanol projects took into account potential grid connection.

Energy demand

The process parameter comparison in chapter 8 showed that on average the microplant requires more electricity than other CO2-based methanol production processes reported in literature. Although the latter are often simulations and never based on actual pilot projects, it is imaginable that microplants are faced with some challenges when it comes to the energy demand. One reason is that optimisation of the most energy intensive process, the electrolysis of water to produce H2, is likely less costly per kilogramme of methanol on the macro scale than on the micro scale. The developers at ZEF explained that optimisation of the AEC unit is possible even today but that the costs of the individual microplants would increase above the target price. Macro-scaled projects such optimisations might be financially relevant but not as significant. As example, Rosental et al. (2020) assume a much lower energy need per kg of H2 in their centralised CO2-based methanol system.

A particular benefit of the microplant is that it co-captures water at high purity. This eliminates the need for separate high purity water production which, according to Biernacki et al. (2018), is associated with a high energy demand and thus high impacts.

Material demand

As discussed in the interpretation chapter, the microplant approach to methanol production requires more materials (minerals, metals, plastics) on average than conventional methanol. The question is whether the same effect would be applicable to the comparison of microplant CO_2-based methanol with macro-plant CO_2-based methanol. If the latter would run on electricity from a photovoltaic plant, one should expect to see a similar energy-related material demand. In this case, this would entail similar requirements for aluminium, silver, and silicon. Of course a CO_2-based macro-sized plant would also require an additional H_2 production facility, and an array of DAC units to capture CO_2, all of which put an additional strain on the material demand. The only difference could be the demand for copper and nickel which can be expected to be more densely present in microplants due to the higher density of control systems and the cost-effective but nickel-intensive AEC units. Rosental et al. (2020) showed that in their analysed system the added material demand from the H_2 production and CO_2 capture facilities resulted in similar trade-off effects observed within this study. Unfortunately, the magnitude of the material demand cannot be compared on basis of the literature results alone.

Micro vs. Macro

As can be seen in this very brief overview, there are arguments in favour of both the microplant concept and centralised macro-scale CO_2-based methanol production. Any resulting differences in the impact profiles of methanol produced via both routes will be a matter of overall process energy efficiency, material use, and access to low-impact electricity. It seems that the microplant approach only applies to the latter and that centralised production may win in the other two areas, though especially for material use additional research might lead to surprises.

9.3. *Research recommendations*

During the course of this project, limitations were identified that were reformulated in opportunities for continued research. This resulted in four potential topics for both academic research and developmental research at ZEF BV.

1. Assessing the severity of impacts, both on an abstract and practical (local) level
In Life Cycle Assessment, normalisation and weighing is sometimes applied to assign a sense of magnitude and relevance to impact scores. Neither are used in this study, mainly for the reason that normalisation still requires a value judgement about the severity of impact scores in relation to another reference. Such references are often on a regional or national scale (e.g. 'compared to the methanol market mix in the Netherlands'). The problem with such thinking is that it bases the judgement on an aggregation of impacts that occur in various places globally, omitting the relevance of local impacts.
To understand the impact that the microplant has on ecosystem quality and human health, it is necessary to identify large single-source emissions in the production chain and to investigate its actual practical implications. This coincides with some of the main challenges of LCAs, and a revised research methodology would be advisable. As such research would require more certain data, the practical assessment of impacts should take place before market introduction, when pilot-scale data is available.

2. Researching DAC emissions and their impacts as critical part of future research
The emissions of the DAC stand for perhaps the most uncertain factor in this research project. So far any experimental data regarding the real-life degradation mechanics is lacking, demanding an approximation based on rough estimations. Although the research into various adverse amine-related emissions for point-source (PS) capture is widely studied, practically no research in this topic could be found for direct air capture. Yet, degradation in DAC systems cannot be expected to mimic degradation in PS systems. For one, nitrosamines are often produced in contact with mono-nitrogen oxides (Dai et al., 2012) which are widely present in flue gasses but not in ambient air. Secondly, the specific poly-amine used in the DAC of ZEF is likely more stable than shorter amines that have been used in PS systems (e.g. MonoEthanolAmine) (Gowda, 2020). The conditions in the DAC system furthermore determine the oxidative and thermal degradation in vastly different ways than in PS systems. Though this project clearly did not aim to define exact damages and damage pathways, it did indicate that DAC emissions might be a problem for human health and ecosystem quality. Further research into the DAC emissions, and mostly the type and volume thereof, is *critical* for the overall assessment of the sustainability of the microplant and could help progress the state of knowledge about DAC systems.

3. Microplants vs. macroplants: opportunity for higher level in-depth LCA studies
In this study CO_2-based methanol from the microplant was only compared with conventional methanol. A preliminary discussion on its potential performance versus centralised 'macro'-scaled CO_2-based methanol projects was possible on the basis of the cross-study analysis. Still, cross-study comparison cannot reach the same kind of deep interpretation and discussion that is possible with comparative life cycle assessment, which has also been discussed as a limitation of this project. A clear opportunity is therefore identified for further academic research into the performance of micro-(decentralised) and mass producible energy technologies vs centralised macro-scale technologies. Alternatively, the general high level discussion on the environmental and/or technoeconomic implications of the decentralised energy technology movement may be promising material for future thesis projects.

4. Life cycle assessment as continuous tool for the technological development of the microplant
The early technological state of the microplant inevitably leads to large uncertainties of all findings in this report. As more research takes place both within and outside of ZEF in relevant topics, the general uncertainty will gradually decline. Life Cycle Assessment can then prove to be a valuable tool to periodically review the environmental performance of the microplant. Upon the availability of new data, this of course specifically applies to major design iterations, such as changes in microplant-size or the addition of batteries. The work produced in this project can form the foundation of newer LCAs.

10 Conclusion

10. Conclusion

The technology start-up Zero Emission Fuels B.V. has designed a small-sized air-to-methanol plant that stands for a novel approach to low-carbon methanol production that is characterised by mass-producibility, potential for upscaling, autonomous remote operation, and dedicated integration with a photovoltaic energy system. To validate whether these potential benefits are extended to the environmental profile of the produced methanol, a cradle-to-gate ex-ante life cycle assessment was performed examining the production of methanol in a 'microplant-farm' configuration of 3250-4000 units in Oman. The study included the assessment of multiple future technology scenarios based on consistent reasoning building on pessimistic, neutral, and optimistic expectations of the technological development of the microplant concept. These scenarios were complimented with the ex-ante modelling of the photovoltaic technology that generates electricity for the microplants. Temporal consistency between the fore- and background was ensured by using the available and most recent future background LCI database.

The exact formulation of the research objective is detailed in the introduction but encompasses 1) the initial comparison with conventional methanol, 2) the highlighting of important impact contributions, 3) the relevance of future technology scenarios, and 4) what other LCA studies can tell us about the position of the microplant in relation to other reported impact profiles. This final section collects the most important findings related to these objectives.

A negative cradle-to-gate climate change impact score
Regarding the first objective, the impact assessment of the future PV-powered air-to-methanol plant shows it is likely that methanol produced using this approach will exhibit a low climate change impact along its production chain. Especially compared to conventional methanol produced via the steam reforming of natural gas, the microplant approach can be associated with a clear climate change mitigation potential. The analysis in this study furthermore demonstrates that the temporary sequestration of CO2 in methanol leads to a negative impact score at the factory gate between -0.92 and -1.09 kg CO2 equivalent per kilogramme of methanol compared to 0.64 kg CO2 eq. for NG-based methanol. If the inevitable re-emission of captured CO2 is considered, for example via combustion, the climate change impacts will lie between 0.29 and 0.47 kg CO2 eq., compared to 2.01 kg CO2 eq. for conventionally produced methanol.

Although a distinct benefit in the climate change category is identified, other impact categories indicate potential adverse effects on ecosystem quality and human health compared to conventional production. Depending on the analysed technological development scenario and their key assumptions, the microplant-methanol shows significantly higher impacts (i.e. >200%) in between five and nine of the twelve analysed environmental impact categories. Specific higher impacts can be found in the freshwater ecotoxicity category (240% increase from NG-based methanol under the ST-N scenario), freshwater eutrophication (270%), carcinogenic effects (560%), non-carcinogenic effects (626%), and respiratory effects (240%). Additional benefits can be expected in the categories of ozone layer depletion (18%) and photochemical ozone creation (81%).

The relevance of a higher mineral and metal demand
The analysis into the impact contributions revealed a high relative importance of the total material demand in the assessed and incumbent methanol production routes. The microplant approach towards low-carbon methanol production is associated with a strongly increased material demand for metals and to a lesser extend for plastics. For one, supplying the high energy demand for the capture CO2 and production of H2 with electricity from photovoltaic panels is responsible for a large part of the material demand. In addition, a significant strain on the material demand originates from the required production of thousands of microplants, including their subsystems, to reach significant production volume. In this study it was analysed that under the short term neutral technology scenario the microplant approach approximately demands between 1-2x more iron, 4-6x more copper, 9-12x more aluminium, and 17-18x more nickel per kilogramme of methanol. Such additional demand was consistently found for other minerals and metals such as lead, silver, cobalt, zinc, tin, and platinum, and for a variety of plastics. As the microplant is still in early development, these numbers are faced with large uncertainties, yet provide a valuable first indication main differences with conventional methanol.

The added material demand as main contributor to environmental trade-offs
Steel for the subsystem parts, copper for the wiring and control systems, and nickel for the electrodes in the alkaline electrolysis unit contribute most significantly to impacts *related to microplant manufacturing* across all categories with specifically high contributions for steel in the carcinogenic effect category (53%), copper in the non-carcinogenic effects and freshwater eutrophication category (46% & 32%), and nickel in the acidification category (40%). Relative to comparable studies, the impacts associated with the generation of electricity are rather low due the high PV panel output under high solar irradiation, updated inventories, and the direct integration of the microplants in the PV plant. Still, electricity-related impacts dominate in the freshwater ecotoxicity (76% of total), (non-)carcinogenic effect categories (56% & 78%), and respiratory effects categories (67%). In all other categories, electricity-related impacts generally are related to about half to the total impacts. The LCA presented in this work thus confirms again the hypothesis from previous works that the climate change impact of CO2-based methanol is linked closely to the impacts of the chosen means of electricity generation.

The capture of CO_2 puts an additional strain on the environmental profile beyond climate change
The degradation of polyamine sorbents in the process of capturing CO_2 highlights a potential environmental hotspot. Using a scenario-based approach, and relying on rough estimates about the implications of sorbent degradation for emissions of ammonia, the results showed that such emissions are significant in the overall environmental profile and lead to potential damages on ecosystem quality and human health. Low sorbent-lifetimes of under 1-2 years cause significant additional burdens both due to emissions and the demand for additional sorbent manufacturing. Of the non-electricity impacts and under the default technology scenario, direct emissions of ammonia contribute 18%, 43%, and 24% respectively to the freshwater & terrestrial acidification, terrestrial eutrophication, and respiratory effects impact categories. The production of the sorbent is furthermore relevant in marine eutrophication with 14.5%. Both contributions are highly dependent on sorbent lifetimes. The current study is too limited to scope the extend and severity of DAC-related impacts and to recommend appropriate mitigation strategies. It has nonetheless shown that these emissions cannot be overlooked and should be subject of future research.

The technology scenarios only result in minor changes to future impacts
The pessimistic and optimistic scenarios that encompass the most likely variations in future performance create only a relatively narrow impact range around the impact results of the neutral scenarios. This effect is more prevalent in the medium term than the short term where the pessimistic scenario assumes little to no technological improvement from the current lab/pilot-scale design, leading to a high impact scores that stretch the impact ranges in all categories. In this scenario this is caused by the low sorbent lifetime and resulting emissions, the high nickel content in the AEC unit, and overall high energy demand.
Subsystem energy efficiency improvements in the technology scenarios generally have the largest influence on results. This is followed by overall technological improvements in PV manufacturing and performance, which reduces impacts across all categories with -13% on average (st.d. 5%). The background scenarios (i.e. global material and energy improvements) are of negligible importance across all categories.

Methanol from the microplant has lower or similar climate change impacts compared to reported impacts of CO_2-based methanol projects in literature
As part of the final research objective, a side-by-side comparison between the results of the LCA in this study and the results of LCAs in comparable literature revealed that methanol from the microplant has a lower-than-average Climate Change impact score and therefore shows potential to be competitive in this category. However, the total energy demand for the production of one kilogram of methanol is higher than average in the short term technology development scenario, and slightly above average on the medium term technology development scenario. It is therefore likely that the microplant thanks its favourable position to the low carbon intensity of the photovoltaic electricity supply. Still, this benefit should not be downplayed, as of all reported systems (n=17), the microplant is the only one to be designed specifically with the intermittency of photovoltaic electricity in mind. The low carbon intensity of the electricity supply is therefore unique to this study and would not be applicable for standard CO_2-based methanol projects. Other, mostly electrochemical, technologies that claim to be suitable for intermittent renewable electricity, still show much higher impacts compared to their thermochemical counterparts such as the microplant.
The comparative environmental performance in other impact categories could not be conclusively assessed due to lacking consistency in both the methodological and technological foundations/reporting of analysed literature. Yet, initial side-by-side comparison with two other studies showed trade-off both in the same

categories and of similar magnitude. Regardless, from the reviewed literature no insights could be identified that signal valid counterarguments for the pursuit of the microplant-approach. It is likely that under the right conditions the microplant is a viable contender for other CO_2-based projects though an additional comparative LCA is required to validate this claim.

Design changes and further developmental research could soften the environmental trade-offs
To mitigate the disadvantageous differences between the environmental profiles of microplant-methanol and conventional methanol a number of strategies can be adopted in the areas of energy demand, energy supply, material use, and CO_2-sorbent upgrading/emission prevention. Energy optimisation remains a key focus for the developers though literature review indicates that the energy demand of the microplant is higher (around 10-20%) compared to other CO_2-based methanol systems. Previous LCA works highlight the opportunity and value of heat integration and AEC efficiency optimisation to mitigate impacts. On the supply side, opting for low-impact energy mixes for PV production and consulting PV environmental profiles may offer additional prospects.
As there is simply a larger material demand for the subsystems and control systems, optimisations beyond the reduction of Nickel are more difficult to envision in this area and the developers are generally recommended to consider the importance of materials and to continuously seek opportunities for material optimisation.
Lastly, optimising the CO_2-sorbent to reduce degradation and prolong its lifetime would both limit emissions and production-related impacts. Alternatively, washing systems commonly applied in point-source capture could be integrated in the microplant to limit the emissions of ammonia.
Overall, the combination of impact mitigation efforts will make it less probable that significant trade-offs in two of the twelve impact categories will occur. In four out of twelve categories however, neither mitigation efforts nor the general optimistic technology scenario will be enough to turn the impact score in favour of the microplant. The relative severity and importance of these trade-offs will need further research.

This study gave a first look at the environmental profile and flagged hotspots, though more research is required
In this research project, a microplant concept for low-carbon methanol production was analysed that is awaiting the move to full pilot scale. It remains a real possibility that process parameters such as the energy demand are underestimated, that the overall process emits gasses that were not yet estimated/included in this study, or that gases are emitted that currently lack characterisation factors.
As the microplant progresses to higher technology readiness levels, both experimental primary data and technology expectations will predict the eventual future performance and emissions with increasing accuracy. Life Cycle Assessment should then be used to continuously evaluate the environmental significance of updates throughout the development trajectory.

Promise and potential of the microplant approach to low-carbon methanol production
If the microplant approach to methanol production from captured CO_2 lives up to the neutral or optimistic expectations set forth in this study, it will prove to be a promising low-carbon pathway to supply the increasing demand for methanol. Yet, like any emerging technology, environmental trade-offs may lure in the shadows of technological development. Only continued attention to the highlighted topics in this report may guarantee its wider sustainability.

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