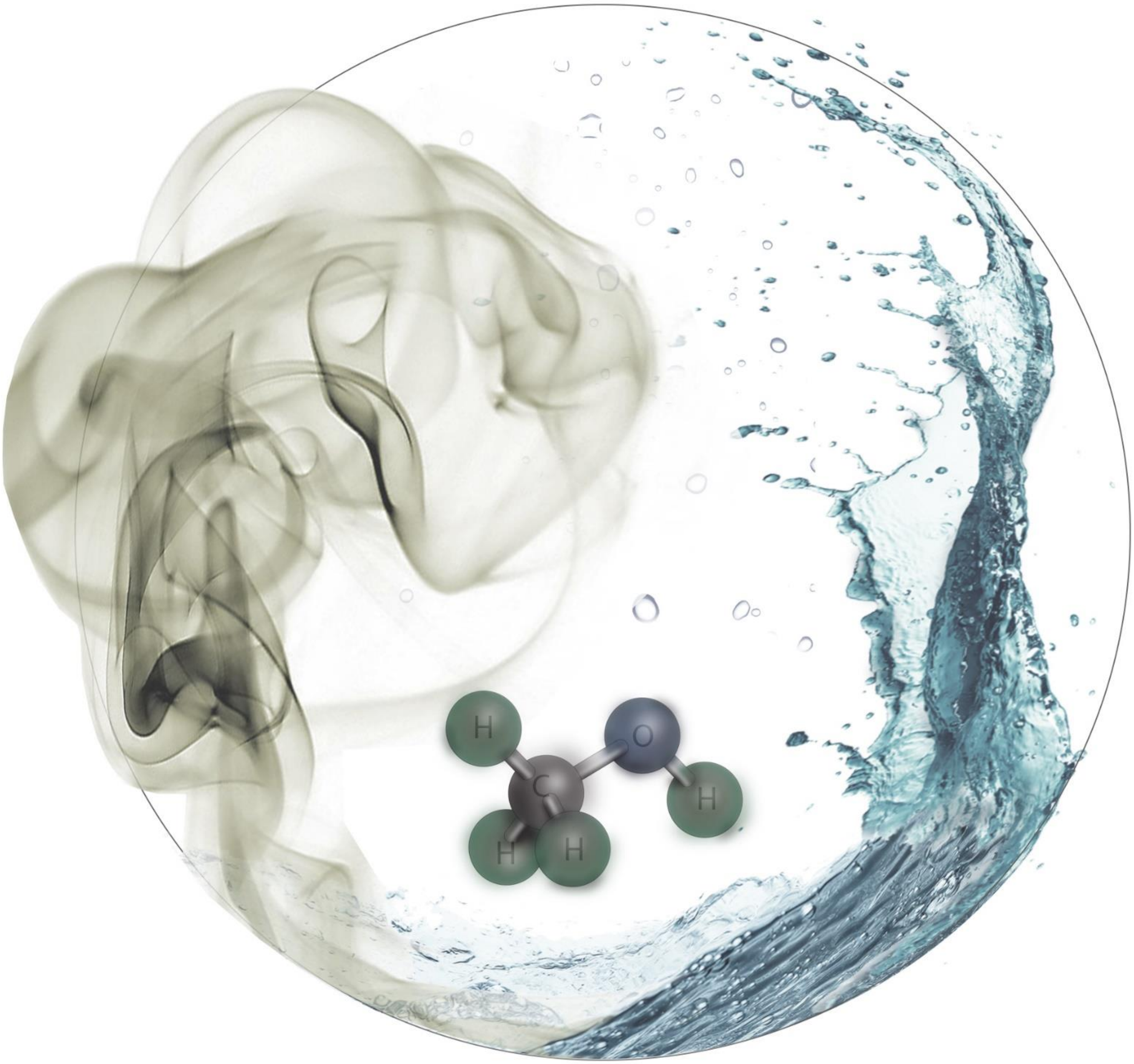

Electrochemical synthesis of CO_2-methanol utilizing direct air capture, CO_2 electrolysis and H_2O electrolysis. A life cycle assessment.

Stanislava Borisová

Universiteit Leiden

INDUSTRIAL ECOLOGY
INNOVATIVE BY NATURE

TU Delft
Delft University of Technology

Master Thesis MSc Industrial Ecology

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A life cycle assessment

Stanislava Borisová

stani.borisova@protonmail.com

1822217 & 4690966

Supervisors:

Dr. S. Cucurachi, CML, Leiden University

Prof.dr.ir. C.A. Ramirez Ramirez, TPM, TU Delft

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This thesis represents my final project within the master's program Industrial Ecology. My motivation for starting this program came from a desire to get an understanding of how the industry works and what can be done to make it environmentally friendly. I am happy to have had the opportunity to learn that and a lot more.

I would like to thank my supervisors, Dr. S. Cucurachi and Prof.dr.ir. C.A. Ramirez Ramirez, for their assistance on this project. I appreciate your optimism and understanding in times when things were not going smoothly. I also thank you for your suggestions on relevant literature, for sharing your expertise on LCA and technology behind CO_2-methanol production and for all your feedback.

Through this thesis, I learnt a lot about assessing real-life technology via LCA and about the functioning of such technology. I also learnt that LCA results depend on so many variables, starting with the quality of input data, through modelling choices, software used and assessment methods selected, that it is important to be somewhat sceptical when reading or interpreting these results and to search for information behind them. And most of all, I learnt that sometimes things don't work, no matter how hard you try.

Because of that, I would really like to thank everyone who was there for me in the past few months. I'd like to thank Carlos Blanco and Mathieu Delpierre for inspecting my model flow-by-flow and for trying to make it work when it didn't. I'd also like to thank Waste4ME for being flexible with my working hours when I needed to dedicate more of my time to this thesis and for finding time to read my chapters. A big thank you goes to my mum for being so supportive and loving. I also thank my sister Alexandra for taking the time to design a beautiful cover page for this document.

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Abstract

This thesis examines the production of an alternative liquid hydrocarbon fuel, namely CO_2-methanol, produced utilising DAC, CO_2 electrolysis, H_2O electrolysis and thermo-catalytic synthesis. The reason for such research lies in a persistent growth in global energy demand, a significant share of which comes from liquid fuels, in the present context of global climate change.

We answer the main research question 'What is the comparative environmental performance of DAC methanol, natural gas methanol and biomethanol?' by meeting three research objectives. The first objective provides a two-level analysis of the mass and energy flows within the system and opens the black-box process of the DAC. The second objective leads to undertaking a life cycle assessment of CO_2-methanol. Last, the third objective evaluates the suitability of LCA for the environmental assessment of realistic industrial processes.

The results of objective one show that mass and energy balances on the DAC process contain inaccuracies and help to identify unknowns in the remaining parts of the CO_2-methanol production. The second objective illustrates that the CO_2-methanol performs better than fossil methanol and biomethanol in terms of climate change impact and land use. Additionally, CO_2-methanol causes a lower extent of environmental impact on human toxicity (non-carcinogenics) and resource depletion (water) in comparison with biomethanol, however, scores worse on these impact categories when compared with fossil methanol. The environmental performance of CO_2-methanol inferior compared to both biomethanol and fossil methanol in terms of freshwater ecotoxicity, human toxicity (carcinogenics) and resource depletion (mineral, fossils, and renewables). Finally, the third objective points to imperfect LCA software available, not sufficient to model realistic industrial processes.

Contents

1. Introduction

The functioning of the world's society is, to a large extent, based on energy usage. Although a rapid fall in energy intensity has been recorded, meaning that on a global scale we are using primary energy more effectively, further growth in energy demand is forecasted for the upcoming 25 years (BP p.l.c, 2018). A part of it will originate from continued population growth. However, a larger proportion of the rise in energy demand will be linked to increasing prosperity in emerging countries, translating into a persistent growth in the global GDP (Van Geuns, 2019). More specifically, an annual growth of 3.5% in GDP is forecasted, largely offset by a 2% fall in energy intensity, leading to a rise of 1.5% p.a. in primary energy demand (BP p.l.c, 2018). In primary energy, a significant role is played by fuels, still dominated by fossil resources (van Geuns, 2019), namely by oil, coal and gas (BP p.l.c, 2018).

The main sectors using primary energy are industry, transport and the building sector (BP p.l.c, 2018). There has been an ongoing discussion on transport and its impact on global climate change. Transport has been contributing to the greenhouse gas emissions significantly: only CO_2 emissions originating from fuel combustion accounted for 36% of total global emissions in 2012. Additionally, this level of emissions is predicted to remain steady through 2040, globally (U.S. Energy Information Administration, 2016).

Presently, 94% of the fuels used for transportation derives from fossil oil (BP p.l.c, 2018), dominated by gasoline, diesel and jet fuel (U.S. Energy Information Administration, 2016). Liquid fuels hold a stable position despite shifts in fuel mix towards renewables (van Geuns, 2019). Such shifts can be ascribed to efforts to manage environmental challenges of fuels, especially emissions of carbon dioxide, but also contaminants, such as sulphur dioxide, nitrogen oxides and mercury (Maroto-Valer, Song, & Soong, 2002). Nonetheless, the shifts towards renewable fuels are rather gradual, as the established transport infrastructure has operating lifetimes of 30 years and more (Davis, Caldeira, & Matthews, 2010), preventing a rapid large-scale adoption of fleet fully powered by renewables.

The necessity to tackle global climate change in an idle infrastructure, while simultaneously providing quantities of fuels demanded, has led to a search for new alternative fuels. Role of such fuels would be meeting the growing demand – from 104 quadrillion Btu of energy consumed in 2012, to 155 quadrillions Btu in 2040 (U.S. Energy Information Administration, 2016) – before transportation experiences a significant shift towards a more sustainable fleet.

1.1 Search for fuel alternatives

Research into potential fuel alternatives commenced as the need to switch from fossil fuels became more prevalent. The possibilities introduced range from conventional to more radical ones. For instance, Daggett, Hadaller, Hendricks, & Walther researched the potential of biofuels and synthetic fuels made of "coal, natural gas and other hydrocarbon feedstocks" in aviation (pg. 1, 2006), under the umbrella of NASA. Considering that their research was driven by the negative reputation of fossil fuels, their choice of fossil feedstocks for synthetic fuels seems contra-productive. Nevertheless, in their later study, this research group chose to focus on biofuels and steer away from fossil fuels (D. L. Daggett, Hendricks, Walther, & Corporan, 2008).

Another alternative partially based on fossil fuels is co-pyrolysis of biomass and coal, researched by Atsonios, Kougioumtzis, Grammelis, & Kakaras (2017). Although the primary goal of this study was to increase the pyrolysis process yield, the authors also advocated for a decreased carbon footprint. While the system met its secondary goal in lowering the carbon dioxide emissions, partially by using biomass and partially due to restricted oxygen inflow, this fuel production method promotes a continued usage of fossil fuels.

Moving away from fossil fuels, various alternatives employing renewable energy sources emerge. For instance, Trieb, Moser and Kern (2018) suggest producing liquid hydrocarbons from solar energy and biomass to provide fuels, such as synthetic diesel and kerosene. They design a small-scale plant, using a combination of renewable energy technologies comprised of concentrating solar power, biogas engine processing sewage and agricultural waste, PV plant, wind power and hydropower. In addition, the proposed plant takes advantage of multiple recycling loops to increase its efficiency and reduce energy requirements. However, the environmental performance of this fuel manufacturing process is not examined, leaving a gap for further research.

1.2 CO_2 to fuels

Another production route for alternative transportation fuels studied is carbon capture and utilisation (CCU). This technology utilises carbon dioxide emissions and converts them into liquid hydrocarbons. In line with above-mentioned liquid hydrocarbons based on solar energy and concurrently exploring CCU options, McDaniel and Bernhard (2010) proposed to harness solar energy in Sahara, Arabian and Gobi deserts, and use it in fuel production. As a feedstock for so-called solar fuels, they examine acids, carbon dioxide in combination with water, alcohols, and water itself, and evaluate the suitability of each feedstock. Their paper is rich in process engineering data but does not consider environmental sustainability. Similarly, Xiong, Kuang, Lin, Lei, Chen, et al. (2018) promote solar fuels production from carbon dioxide as a way of mitigating GHG emissions. They develop a novel twin reactor and compare usage of various catalysts to improve the process performance. Nonetheless, their study also lacks an environmental assessment of such manufacturing process.

To the author's knowledge, the study of Van Der Giesen, Kleijn, & Kramer (2014) is the first to compare the environmental performance of solar fuels from CO_2 to other alternatives via Life Cycle Assessment (LCA). They conclude that these combustibles require a substantial amount of energy to be produced, as carbon dioxide is mostly available in diluted form, and in terms of energy requirements perform worse than fossil-based diesel and gas-to-liquid, bio-based ethanol and biomass-to-liquid, and solar-based hydrogen (Van Der Giesen et al., 2014).

Fernández-Dacosta, Shen, Schakel, Ramirez and Kramer (2019) examine the environmental performance of various CO_2-based fuels. They consider the end-of-life emissions to demonstrate the short time of CO_2 capture in these fuels and the debatable decarbonization potential. They indicate that the most problematic aspects of CO_2-based fuels are hydrogen supply dominated by fossil fuels and limited hydrogen electrolysis capacity, which would allow for renewable sources utilisation. According to this study, some of the most promising liquid fuels for transportation are dimethyl ether (DME), methanol (CH_3OH) and ethanol (C_2H_5OH) (Fernández-Dacosta et al., 2019). Additionally, a study by Daiyan, Lu, Ng, & Amal (2017) also suggested producing formic acid (HCOOH).

The focal point of this thesis is CO_2-methanol, as it has a potential to replace gasoline, and to lower emissions of direct CO_2 considerably more than other alternative fuels (Fernández-Dacosta et al., 2019). This is in line with a so-called methanol economy, in which carbon dioxide emissions are utilised for methanol forming. The advantages of large-scale methanol production include its capacity to store energy, usability as a fuel, and potential to produce other chemicals, such as ethylene and propylene from this chemical (Olah, 2005). Additionally, it is a safer alternative to hydrogen, and also more convenient, since it comes in liquid form, thus does not require liquefaction (Olah, 2005).

Nowadays, methanol is being produced via catalytic reforming of fossil fuels, illustrated in Figure 1.1A. To get liberated from fossil fuels, CO_2 routes to produce this substance have been researched. While CO_2-methanol is already being produced on a large scale by thermochemical synthesis, recently, there have been developments in manufacturing CO_2-methanol via electrochemical synthesis, the latter shown in Figure 1.1B. Such production route consists of three main processes, namely CO_2 electrolysis, utilising a previous carbon dioxide capture; H_2O electrolysis and CH_3OH synthesis.

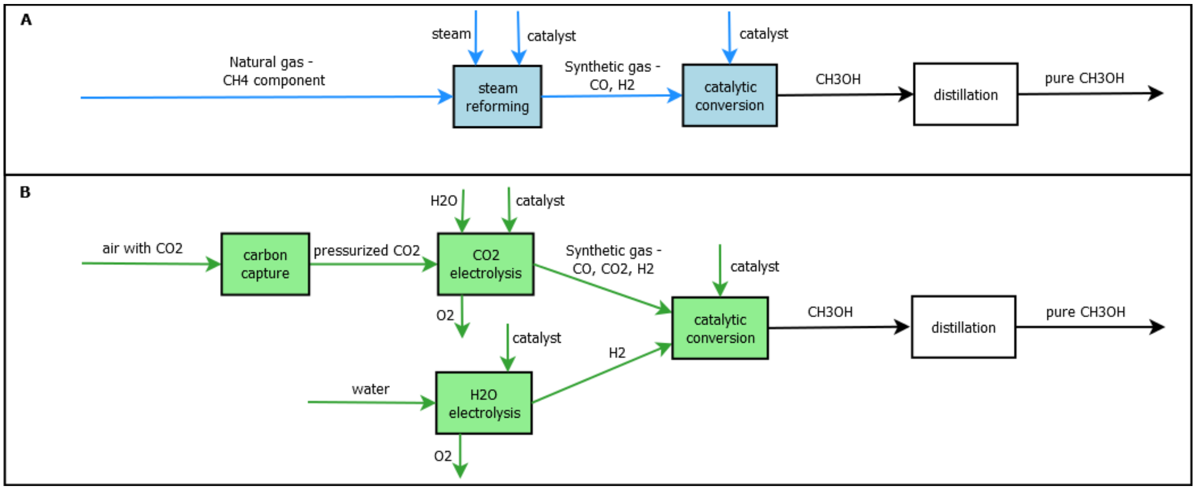


Figure 1.1: Methanol production. A - from methane steam reforming; B - from the electrolysis of captured CO_2.

1.3 Goal of this thesis

Methanol production from carbon dioxide emissions based on electrochemical synthesis is a novel technology, only applied on a laboratory scale. Therefore, there are significant knowledge gaps when it comes to the processes involved. Due to technology novelty and intellectual property concerns, there is a lack of process engineering data. Consequently, environmental impacts of CO_2-methanol are uncertain, as it has not been possible to model its production in-depth, but rather by using an aggregated black-box approach. Because of that, it is important to explore how CO_2-methanol performs in terms of impacts on the environment. This thesis aims to compare the environmental performance of CO_2-methanol to well-established alternatives, namely methanol from natural gas reforming, and biomethanol, produced from biomass. The selection of alternatives reflects that the main driver behind CO_2-methanol production is its assumed superiority in terms of impacts on the environment in comparison with methanol from natural gas reforming and biomethanol.

1.4 Structure of this thesis

This problem introduction is followed by Chapter 2, which provides background information on carbon capture and utilisation and CO_2-methanol production, identifies a knowledge gap, and lists research questions to be answered. Afterwards, Chapter 3 provides methodological choices and relevant theories. Next, analysis of results is given in Chapter 4, followed by a discussion in Chapter 5 and conclusions in Chapter 6.

2. System background and knowledge gap

The following section provides information on the investigated CO_2-methanol production system, as illustrated in Figure 1.1B. Processes are explained in sequential order, from carbon capture to catalytic synthesis of methanol. Afterwards, decarbonization potential of carbon capture and usage (CCU), compared to carbon capture and storage (CCS) is discussed, due to an ongoing debate on environmental benefits of carbon dioxide recycling in fuels. Finally, a knowledge gap is identified, providing a ground for this research, followed by the research question and objectives.

2.1 Carbon capture

As CO_2-based fuels rely on the feedstock of carbon dioxide with the aim of lowering the GHG emissions, these emissions need to be captured. There are multiple ways of capturing the CO_2, some being implemented at the source of emissions, while others extract carbon dioxide from the ambient air. This section examines possible technologies to capture carbon dioxide.

Technologies that are applied at industrial sites take advantage of high CO_2 concentration at the source of emissions, contained in flue gases. Under this approach, we distinguish three main types of carbon capture, namely post-combustion capture, pre-combustion capture and oxyfuel combustion systems. Post-combustion capture consists of CO_2 absorption from exhaust gases; pre-combustion enables capturing carbon dioxide from fuel before its combustion; and finally oxyfuel combustion systems allow for easier CO_2 separation by combusting the fuels in oxygen rather than by air, resulting in flue gas mainly consisting of water and carbon dioxide (The Carbon Capture & Storage Association (CCSA), 2019).

The second group of technologies, also known as Direct Air Capture (DAC), focuses on capturing the CO_2 emissions from the ambient air, despite its low concentrations, namely 400 ppm. DAC belongs to Carbon Dioxide Removal (CDR) technologies. According to United Nations Intergovernmental Panel on Climate Change, all strategies limiting global warming to 1.5 °C rely to some extent on CDR (Rogelj, J., D. Shindell, K. Jiang, S. Fifita, P. Forster et al., 2018). In line with this argument, and to examine its environmental performance, DAC is selected as a carbon dioxide feedstock for CO_2-methanol system inspected in this thesis.

2.1.1 Direct air capture

Presently, there are three main approaches to capturing CO_2 from the air: chemical approach, cryogenic approach, and using membranes (Sandalow, Friedmann, & McCormick, 2018). An overview of different methods and parties active in pursuing them is illustrated in Figure 2.1, below. Each of these three approaches is shortly explained in the following paragraphs.

The most applied DAC approach is the chemical route, where the air is blown into an air contactor on liquid solvents or solid sorbents, which temporarily bind carbon dioxide. Afterwards, the solvent or sorbent gets regenerated, releasing the CO_2 within the DAC facility. Unlike the chemical route, the cryogenic approach to CO_2 capture relies on a high freezing point of CO_2 and is presently implemented in cryogenic oxygen separation (Sandalow et al., 2018). Finally, membranes are capable of isolating carbon dioxide from both the air and seawater (Sandalow et al., 2018). However, the applicability of membranes in DAC is limited due to a lack of driving force, which would allow air to pass through them.

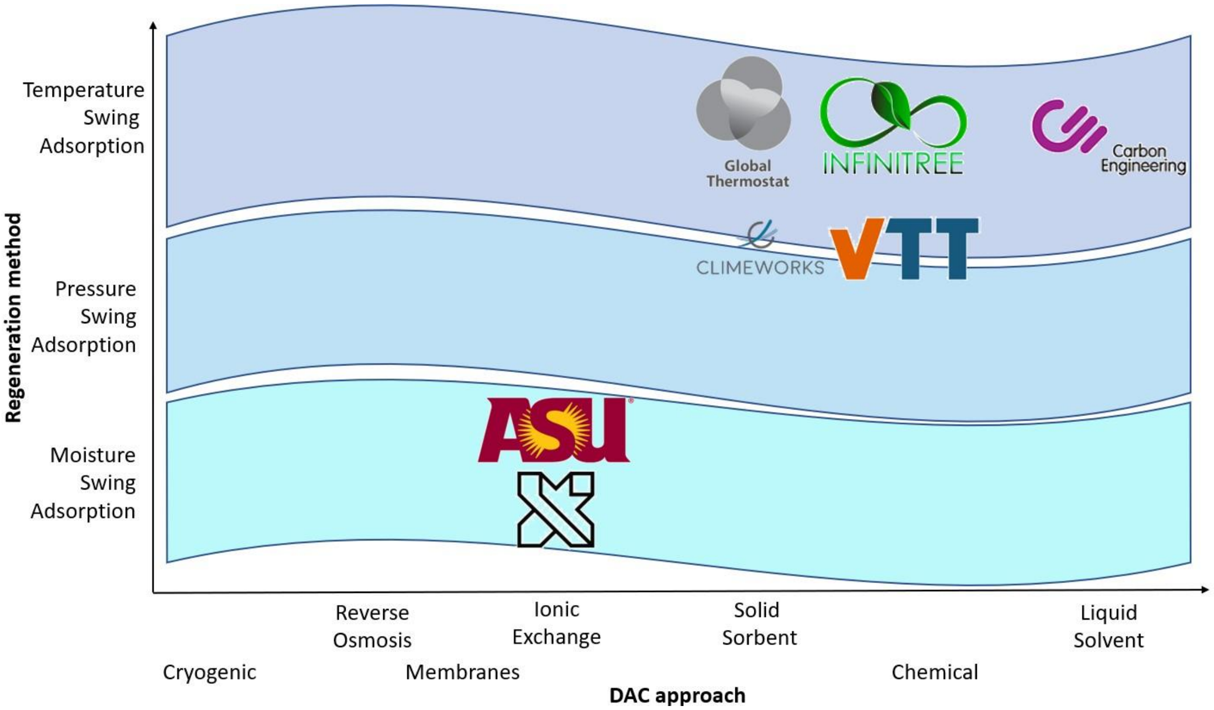


Figure 2.1: DAC actors, categorised based on approach and material used; and regeneration technique. ASU = Arizona State University, X = Project Foghorn, in collaboration with PARC, VTT = Technical Research Centre of Finland

Currently, the companies most active in DAC are Climeworks, Global Thermostat, and Carbon Engineering. As illustrated in Figure 2.1, all these parties capture carbon dioxide via the chemical route. Because the chemical approach to DAC is most applied, we inspect it closer in this thesis.

Chemical route

There are four main categories of sorbents for the chemical approach to DAC, including aqueous hydroxides, solid-supported amines, solid alkali carbonates, and physiosorbent materials (Sandalow et al., 2018). Within the DAC process, sorbent material gets regenerated, releasing the bonded carbon dioxide, and is reused to capture more CO_2. The regeneration itself can be done in three ways. Firstly, by temperature-swing adsorption (TSA), in which the material gets heated, secondly by moisture-swing adsorption (MSA), where humidity levels are altered, and thirdly, by pressure-swing adsorption (PSA), where the ambient pressure is modified (Sandalow et al., 2018).

Due to a relatively low number of DAC systems available and concerns regarding intellectual property, there is a lack of process engineering data describing how carbon dioxide gets captured, released and stored via DAC. A recently published article by Keith, Holmes, St. Angelo, & Heidel (2018) provides the most in-depth process data on DAC so far, reflecting Carbon Engineering's approach based on chemical capture, employing liquid solvent. Their paper serves as a basis for a comprehensive investigation of DAC in this thesis.

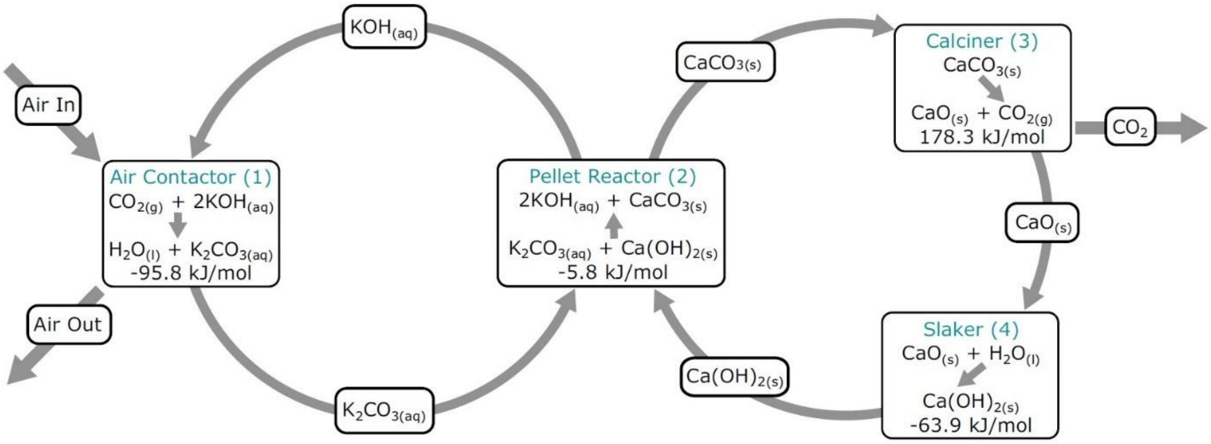


Figure 2.2: Carbon Engineering's DAC technique (Keith et al., 2018)

As can be observed from Figure 2.2, the system used by Carbon Engineering consists of four main parts, namely from air contacting, pellet reaction, calcination, and slaking processes. The system is based on liquid potassium hydroxide solvent, which binds the inflowing carbon dioxide into molecules of potassium carbonate. These molecules enter the pellet reactor, where they form pellets of calcium carbonate. The pellets get decomposed at high temperature into calcium oxide and released carbon dioxide, which compressed and stored or utilised. The high-temperature environment is achieved by natural gas combustion, promoting continued use of fossil fuels.

An environmental assessment of Carbon Engineering's process, formerly based on sodium hydroxide solvent, was undertaken by De Jonge, Daemen, Loriaux, Steinmann, & Huijbregts (2018). In their study, De Jonge et al. (2018) examine life-cycle carbon efficiency, i.e. the ratio of CO_2 captured to CO_2 used for the capture, under three scenarios – baseline, optimistic and pessimistic. Although results differed substantially per scenario, all scenarios resulted in DAC capturing more carbon dioxide than the emission needed to build and run the system itself. Their study focused on DAC to geological storage.

2.2 CO_2 electrolysis

The CO_2 electrolyser, currently operating on a lab-scale, uses carbon dioxide and water as feedstock to produce synthetic gas and a stream of oxygen. Synthetic gas, also known as syngas, contains CO_2, CO and H_2. Including a 4-9% CO_2 content in syngas allows for faster methanol formation (Torri, 2019). Thus, CO_2 electrolysis enables recirculating of carbon dioxide and keeping a relatively constant level of ambient CO_2 emissions.

The main components of the CO_2 electrolyser are a cathode, containing catalyst and catholyte solution; a membrane; and an anode consisting of anode catalyst and anolyte solution. While the cathode aims to reduce the incoming stream of CO_2 into CO, the primary reaction taking place on the anode is oxygen evolution reaction, producing molecules of O_2. The performance of the CO_2 electrolyser depends on catalysts used and choices on catholyte and anolyte, both being liquid solutions recirculating within cathode and anode, respectively.

A substantial amount of research into CO_2 reduction reaction has been undertaken, with different substances used as catalysts, catholytes and anolytes. Figure 2.3, below, provides a short visual representation of different system choices examined, based on a summary by Torri (2019).

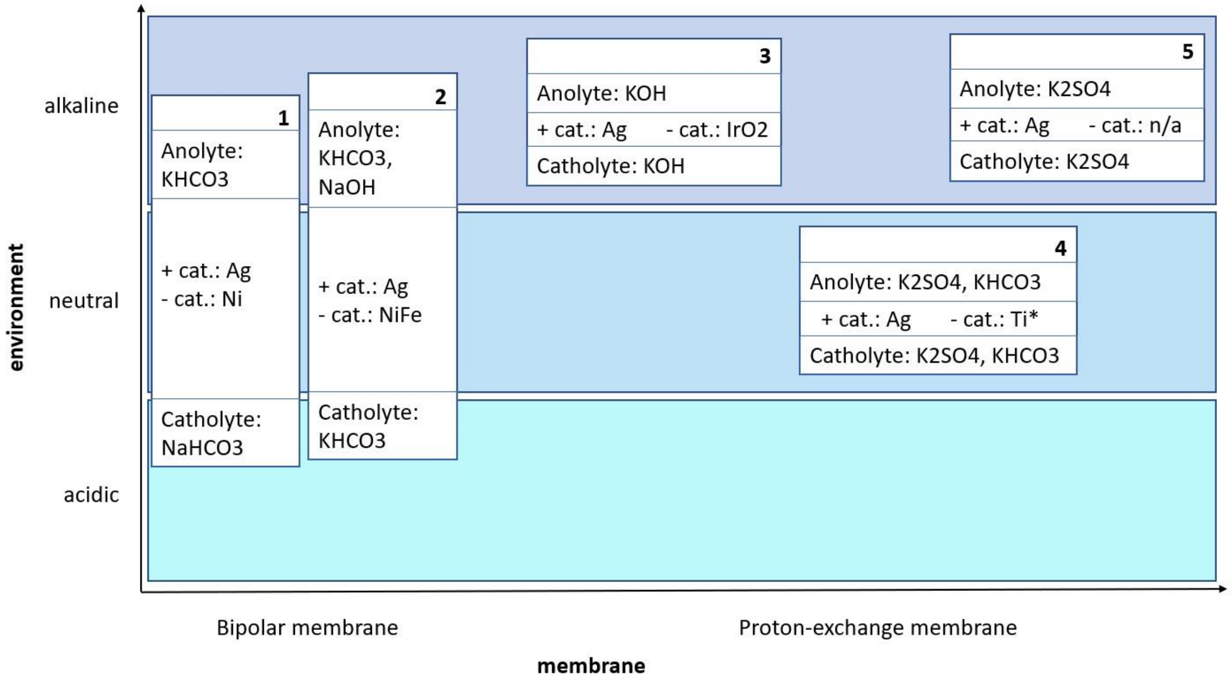


Figure 2.3: Studies on CO_2 reduction reaction, classified by type of membrane and environment provided by the liquid solution. 1 = Salvatore et al., 2017; 2 = Vermaas and Smith, 2016; 3 = Verma et al., 2016; 4 = Haas et al., 2018; 5 = Jeanty et al., 2018. TI = IrMMO-coated Ti.*

The system examined in this thesis is based on the research of Veronica Torri (2019). Her investigation uses rather novel CO_2 electrolysis technology, currently only available on a laboratory scale, and combines it with more established water electrolyser and catalytic syngas conversion, to produce CO_2 methanol. The goal of her research was to provide a techno-economic assessment of such a system. Torri reports rather detailed process data, which were adopted in this thesis.

Torri's CO_2 electrolyser utilises a bipolar membrane. Additionally, the cathode environment is based on a $KHCO_3$ and KCl catholyte solution and an Ag catalyst. Furthermore, the anode environment uses a KOH anolyte solution and a Ni anode catalyst (Torri, 2019).

2.3 H_2O electrolysis

As mentioned above, it is desirable for the final syngas composition to contain between 4% and 9% of carbon dioxide. In her research, Torri (2019) sets the ideal syngas composition for methanol synthesis at a ratio of 9% CO_2, 21% CO and 70% H_2. As syngas produced from CO_2 electrolysis contains a lower quantity of hydrogen, additional hydrogen needs to be produced (Torri, 2019). Furthermore, to keep the environmental impacts of such production low, water electrolysis is suggested instead of conventional natural gas steam reforming process, illustrated in Figure 1.1.

Water electrolysis is a process of splitting water into hydrogen and usable oxygen (Lücking, 2017). There are currently three types of H_2O electrolysis, specifically alkaline electrolysis (AE), proton-exchange membrane electrolysis (PEM) and solid oxide electrolysis cell (SOEC) (Torri, 2019).

Within AE, all feedstock of water enters the cathode, where it is split into hydrogen and hydroxide anion (OH^-) (Holladay, Hu, King, & Wang, 2009). OH^- travels to the anode, where oxygen gets produced, and hydrogen stays in aqueous alkaline electrolyte. This method of water splitting is the most developed one; however, it also has the lowest electrical efficiency and the highest electrical energy costs (Holladay et al., 2009). Still, it is least intense in capital costs required.

During PEM electrolysis, water enters the system at the anode. There, it is decomposed into protons and oxygen. Afterwards, the protons travel to the cathode, where they form hydrogen molecules (Holladay et al., 2009). PEM uses a solid polymeric membrane and is more efficient than AE; however, it is not fully commercially available yet and is rather expensive (Lücking, 2017).

SOEC works similarly as AE, as the process also starts at the cathode, and as "oxygen travels through the electrolyte, leaving the hydrogen in the unreacted steam stream" (Holladay et al., pg. 256, 2009). SOEC is based on a solid ceramic membrane (Lücking, 2017), it is least developed of the three alternatives and faces many system degrading issues and challenges, such as corrosion, necessary seals and thermal cycling (Holladay et al., 2009). Nevertheless, this method of producing hydrogen is the most electrically efficient one.

In the scope of this thesis, alkaline electrolysis is applied due to its high technology readiness level.

2.4 Methanol synthesis

Currently, the majority of methanol is produced via natural gas reforming and through the catalytic conversion of syngas (Lücking, 2017). To lower the impact of methanol production, and to utilise the GHG emissions, an alternative syngas feedstock, such as ambient carbon dioxide studied in this thesis, can be employed. Moreover, recirculation of carbon dioxide in the process also leads to a faster reaction of methanol formation, by up to one 100 times (Torri, 2019). This goes in line with the syngas composition chosen for this thesis. Nevertheless, this method of methanol production is not to be confused with the direct conversion of carbon dioxide to methanol.

Most common catalytic conversion of syngas is a low-pressure catalytic reaction, employing either copper/zinc oxide catalyst with aluminium oxide ($Cu/ZnO/Al_2O_3$) or copper/zinc oxide catalyst with chromium oxide ($Cu/ZnO/Cr_2O_3$). As the former requires lower temperature and pressure conditions, $Cu/ZnO/Al_2O_3$ catalyst is chosen for this system. The output of the low-pressure catalytic reaction is highly pure (>99%) methanol.

2.5 Identification of knowledge gap

Although various studies investigate solar fuels, research focused on CO_2-methanol with a high level of detail is limited due to the lack of process engineering data, made available only to a certain extent and only recently. Therefore, models representing CO_2-methanol production from DAC and utilising electrolysis and catalytic syngas conversion are unavailable, or, in cases where a part of the system is examined, only expressed in terms of aggregated 'black boxes'. Thus, this thesis aims at addressing the following knowledge gaps:

- CO_2 mitigation potential of DAC
    - lack of comprehensive life cycle assessment of DAC
    - little insights into energy and material requirements available
    - recycling loops adopted in industry for higher efficiency not modelled

- LCA of CO_2-methanol production via electrolysis
    - combining a series of novel technologies, which are otherwise separate systems
    - modelling this innovative process, part of which is available in techno-economic assessment, in LCA
    - comparing the results with methanol from natural gas steam reforming and biomethanol

In order to address these knowledge gaps, the following research question needs to be answered:

What is the comparative environmental performance of the DAC methanol, natural gas methanol and biomethanol?

Information necessary will be obtained by meeting the following research objectives:

1. Analyse the mass and energy flows of DAC as described by Keith et al. (2018) with the goal of disaggregating commonly used black box into sub-processes with their respective flows; obtaining high-resolution data for inventory analysis; cross-checking the novel data; and identifying potential uncertainties and inconsistencies.

2. Undertake a Life Cycle Assessment of DAC and CO_2-methanol to quantify their environmental impact, especially climate change potential; and to compare CO_2-methanol with other fuel alternatives.

3. Evaluate the appropriateness of Life Cycle Assessment for modelling high-detail flows reflecting the real-life industrial processes, as modelling multiple recycling loops and composite flows, which reflect chemical reactions, is not a common practice.

The following chapter presents the methodology applied to meet these research objectives and to answer the main research question.

3. Methodology

This chapter provides an overview of the methods applied to achieve each of the research objectives. Even though the structure of this chapter follows the order of objectives as stated in the knowledge gap, the three objectives are closely linked, leading to iteration between them throughout the research process.

In other words, to undertake an LCA, inventory had to be built, for which data analysis was needed. While building the LCA model and running it, several issues came up linked to the complexity of the process reflected in the model, which is why suitability of LCA for the purposes of DAC methanol production had to be evaluated. This then led to a thorough check of the model, alterations, try-outs with more aggregated flows, further evaluation of LCA's suitability for the DAC methanol production case and additional changes to flow modelling. This is shown in Figure 3.1, where the output from one stage of research concerning a particular objective becomes an input for another and also where the input to meet the objective is required from a different research objective.

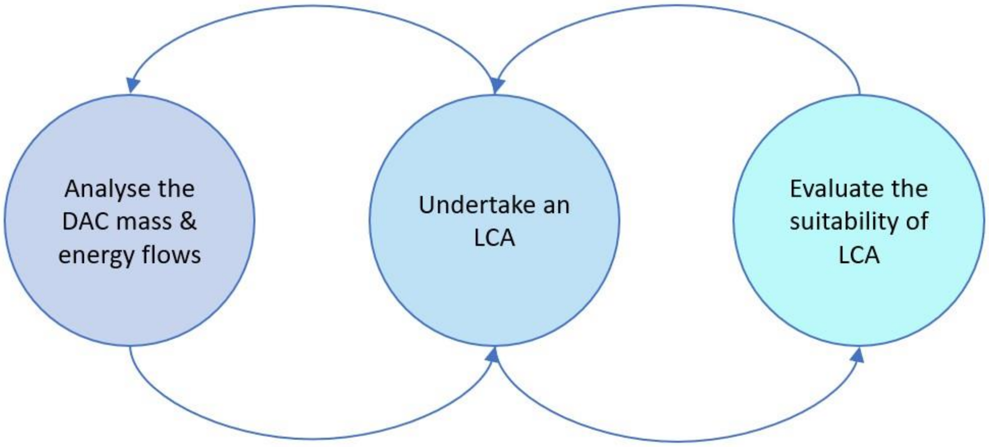


Figure 3.1: Research objectives - feedback loops and iteration of the research process.

3.1 DAC analysis of data from Keith et al. (2018)

Due to the novelty of DAC as technology and related intellectual property issues, data on capturing carbon dioxide via DAC is limited. This is why most studies that evaluate DAC's environmental performance work with a so-called 'black box' approach, and only examine flows that enter and leave the system, yet not the processes within it. As a consequence, a publication by Keith et al. (2018), which reflects DAC system of Carbon Engineering, provides valuable data input for this thesis and an opportunity to undertake a more realistic impact assessment of DAC.

We apply a two-level data analysis, as illustrated in Figure 3.2. The first level investigates flows of mass and energy that enter and leave the system. The second level only applied to the DAC process, offers a deeper look, as it examines flows within the DAC production plant, amongst various parts of equipment and amongst various processes, focusing on chemical reactions that take place. This sheds light into DAC since it opens an otherwise 'black box' system. Moreover, it ensures that the energy and mass flow data published recently (Keith et al., 2018) is cross-checked.

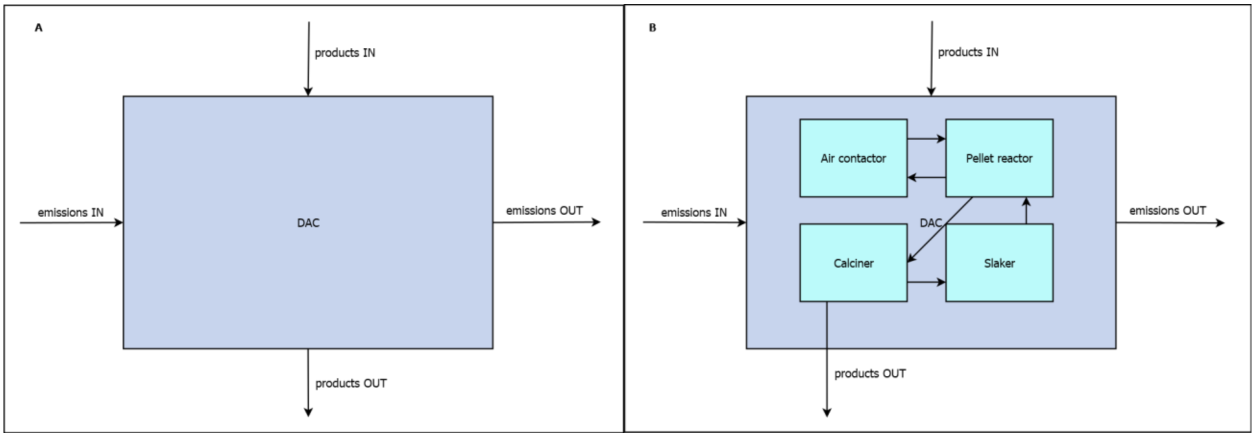


Figure 3.2: A - one-level system analysis, B - two-level system analysis, (simplified).

The second level of the system analysis looks at four main chemical reactions that take place, shown below. Equation 1 demonstrates the reaction of carbon dioxide with a film of potassium hydroxide solvent, which binds the CO_2 molecules into potassium carbonate. This reaction takes place in the air contactor (Figure 3.2B), after which, potassium carbonate flows into the pellet reactor. In the pellet reactor, the reaction shown in equation 2 occurs. Namely, potassium carbonate reacts with calcium hydroxide and produces pellets of calcium carbonate. These pellets flow from the pellet reactor into a calciner, where they decompose into calcium oxide and release carbon dioxide. This is shown in equation 3. Finally, produced calcium oxide reacts with water in the slaker and thereby, necessary calcium hydroxide is produced (see equation 4). Assumptions on actual yield of reactions are based on number of moles available in the mass flows.

Equation 1: binding of carbon dioxide onto the liquid solvent

$$CO_2 + KOH \ \rightarrow H_2O + K_2CO_3$$

Equation 2: calcium carbonate pellet production

$$K_2CO_3 + Ca(OH)_2 \ \rightarrow 2KOH + CaCO_3$$

Equation 3: calcination and carbon dioxide release

$$CaCO_3 \ \rightarrow CaO + CO_2$$

Equation 4: slaking - quick lime production

$$CaO + H_2O \ \rightarrow Ca(OH)_2$$

Flows between other, auxiliary parts of the system, where no reactions take place, are also inspected, assuring that incoming flows are equal to outgoing flows. The system analysis looks into both mass and energy flows. For the latter, it is investigated whether the energy generated in or brought into the system matches the energy consumed. In case that inconsistencies are detected, in other words, if the flows in and out do not balance, additional input required or excess output produced, is calculated.

This analysis provides verified data for modelling the first process of CO_2-methanol production. Unlike the DAC, data on the remaining processes, namely CO_2 electrolysis, H_2O electrolysis and methanol synthesis was more wide-spread and already available at a sufficient level of quality, which is why this level two analysis is not applied to the rest of the system. This is summarised in Figure 3.3, below.

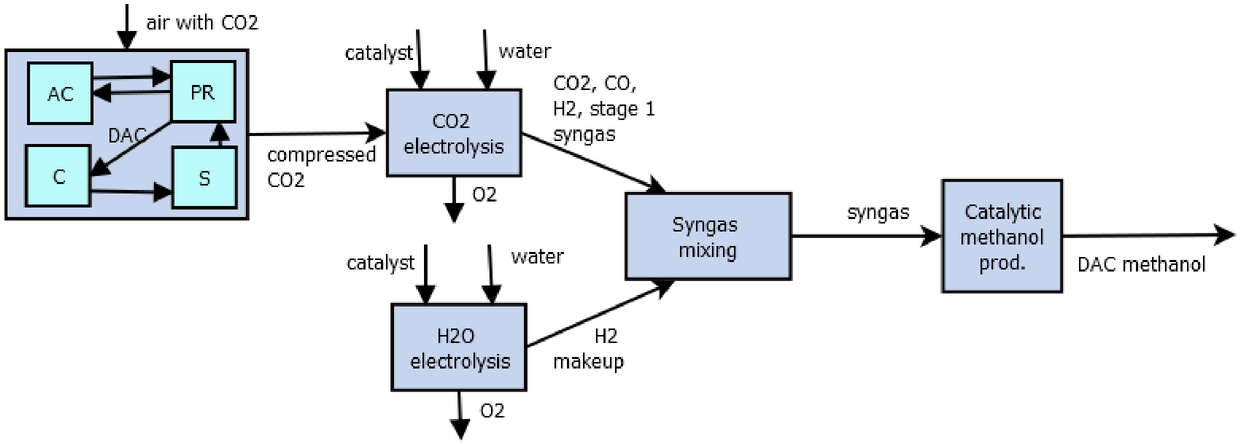


Figure 3.3: An overview of data analysis applied to DAC methanol production, per process. DAC is examined in two levels, while the rest of the system only in one level.

3.2 Life cycle assessment

We apply the tool of comparative life cycle assessment in order to quantify the environmental impact of DAC and CO_2-methanol, and to compare CO_2-methanol with other fuel alternatives. Such LCA also allows for identifying the hotspots, in which most impacts occur. Only environmental sustainability is examined in this thesis.

3.2.1 Goal, scope, function

The LCA is based on the current state of the DAC, as developed by Carbon Engineering, with adjusted material and energy balances (see section 3.1). Additionally, it also applies the novel CO_2 electrolysis technology, as developed at TU Delft, described by Torri (2019), and more established water electrolysis, based on the AE approach. Both electrolyses are powered by electricity from wind turbines. To keep the geographic consistency, it is assumed that the DAC system is installed in the Netherlands, as well as the remaining parts of the production process. This is also in line with the high availability of wind power in the Netherlands.

It is important to mention that the construction of the DAC machinery is excluded from our model due to a lack of information on machinery composition and its weight. For the sake of consistency, materials used for machinery building of the remaining production processes is also not considered.

The LCA examines the production of CO_2 methanol until the well point. The function researched in this LCA is 'providing an alternative fuel option for the current infrastructure'. This is quantified in the functional unit of 16.7 kilotons of CO_2-methanol produced per year. The functional unit was chosen based on the techno-economic assessment done by Torri (2019), where the initial aim was to produce 15 kt/year, reflecting the novelty of the technology. However, a possibility to increase the annual production up to 16.7 kt/year was reached by optimizing the process by applying an additional recycling flow, which is described in Design 3b. The reference flow of this LCA study is 16.7 kt/year of CO_2-methanol to be used in the current transport infrastructure. This reference flow is compared with two alternatives mentioned above, namely fossil-based methanol, which is currently the most established methanol production route;

and biomethanol, fuel which is being adopted for the purposes of better environmental performance compared to fossil-methanol. For the two alternatives, the functional unit studied is also 16.7 kt/year.

The CO_2-methanol plant is based on currently available technologies, which vary in their technology readiness level (TRL). They presently range from a TRL of 7 for DAC (system prototype demonstration in an operational environment), 3 for CO_2 electrolysis (proof of concept), 9 for water electrolysis and 9 for catalytic methanol synthesis (actual system proven through successful mission operations). Nevertheless, the final data reported by Torri (2019) assumes that these subsystems are optimized, reflecting the TRL of 9 throughout the entire CO_2-methanol production process, corresponding to commercial availability. Therefore, the LCA model built reflects this optimized methanol production.

3.2.2 System boundaries and multi-functionality

This section provides an overview of system boundaries, in order to clarify which parts of CO_2-methanol production are part of the research and which fall out of the scope. Addressing the economy-environment boundary, all the foreground processes are part of the economy. When it comes to the environmental emissions, most of them originate from background processes. For some of the foreground processes, such as DAC and CO_2 electrolysis, some emissions that occur are neglected. This is partially due to a high rate of recycling applied to the system and partially due to a lack of data. The economy-environment system boundaries are summarised in Figure 3.4, with light blue arrows for the flows from and to the environment, dark blue for the flows from and to the economy and black for the foreground reference flows within the system.

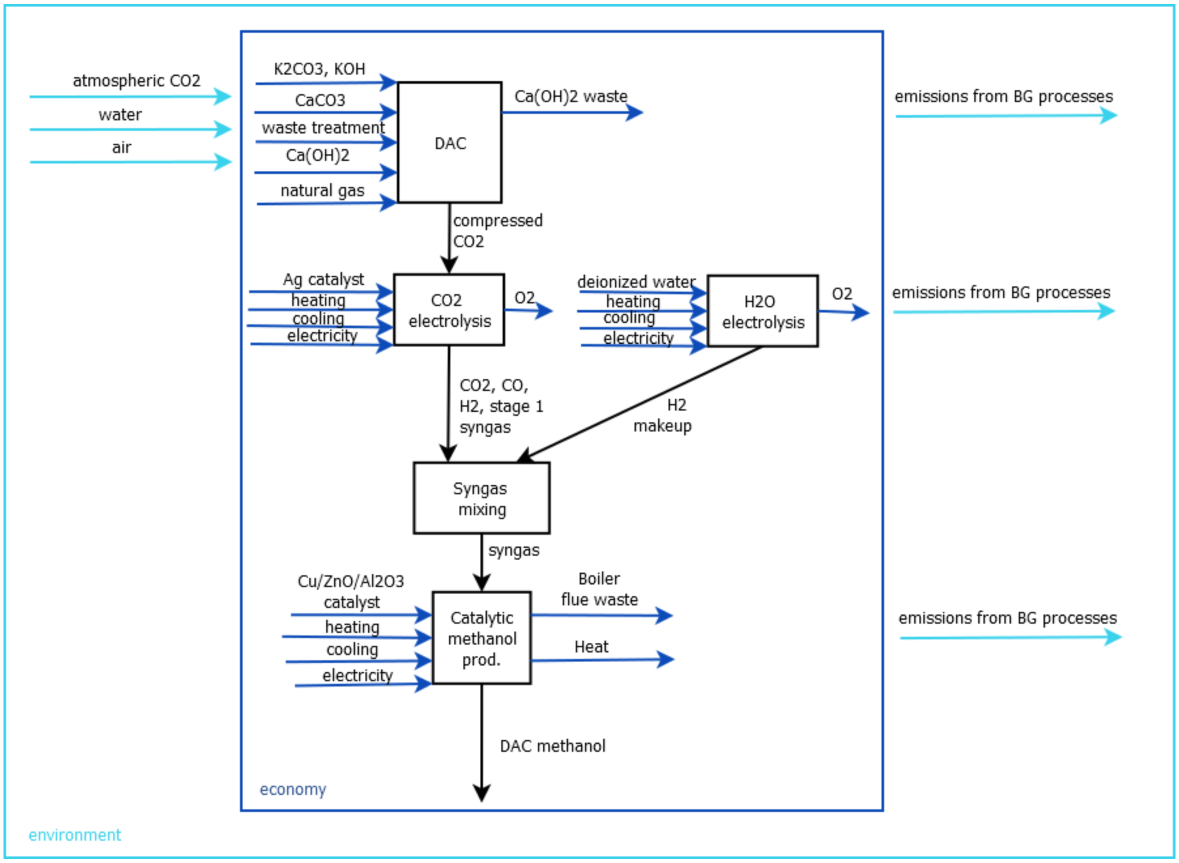


Figure 3.4: Economy-environment system boundary of CO_2-methanol LCA model

When it comes to cut-offs applied in this LCA, machinery is not considered in the entire CO_2-methanol production process. Additionally, some of the steam flows within DAC, namely those within closed-loop recycling, are cut off, as they do not leave the system. Finally, the water applied in the heat exchanger and condensers of DAC is also cut off, as this water does not change the composition of the flows entering the heat exchanger.

Regarding the multi-functionality, many processes within the DAC are modelled as multi-functional. While some of them are of multi-functional nature, since they either produce multiple products or recycle waste streams, several DAC processes are multi-functional due to the modelling approach chosen. For example, air contacting process leads to an outgoing flow of KOH solvent, containing potassium carbonate. This output is then modelled as a stream of KOH, a stream of K_2CO_3 and a stream of water. Nevertheless, all the composite flows are recirculated within the DAC system, and therefore, all the impacts stay inside the process. This choice of modelling composite flows is discussed further in section 3.3.

Furthermore, electrolysers also produce multiple products, with oxygen as a common by-product. Since the main reason for undertaking electrolysis is the production of syngas rather than the production of oxygen, most of the environmental impact are allocated to the syngas flow. More explicitly, the allocation is applied on economic basis, ascribing 60% of impacts to the syngas and 40% to the flow of oxygen, which is in line with the techno-economic assessment of Torri (2019). It is, however, important to note that the infrastructure necessary to store oxygen for further sale, such as liquid nitrogen and storage tanks, is omitted in the model. Lastly, the catalytic conversion of syngas to methanol also produces heat as a by-product. Due to the relatively low economic value of excess heat and the focus on methanol production, economic allocation with a 1:9 ratio is applied, respectively.

3.2.3 Data collection

As mentioned before, DAC data for the LCA model is taken from Keith et al. (2018) due to limited data availability on the DAC process. This data is balanced, where needed, by either adding a missing quantity of a flow or treating an excess quantity. In both cases, the balancing flows come from ecoinvent 3.4 background processes of the model.

Additionally, lab-scale data for CO_2 electrolysis is adopted from Torri (2019), based on the e-Refinery project undertaken by Delft University of Technology. Furthermore, data for water electrolysis and methanol synthesis are also taken from Torri (2019), since her model is the most suitable based on process efficiency, economic cost and environmental performance.

As information on catalysts used in terms of quantity and precise composition is missing in the study of Torri (2019), necessary data is compiled in the following way: total amounts of catalysts in CO_2 electrolysis and methanol synthesis come from an assumption that 1 kg of product (either syngas or methanol, respectively) consumes 0.01 g of catalyst per year. Furthermore, electrolyte quantity for water electrolysis comes from an MSc. thesis by Delpierre (2019), who reported a ratio of 1-2.5 g electrolyte/kg product. The composition of NiAg catalyst used in CO_2 electrolysis is derived from Bettahar et al. (2009) and a ratio of copper, zinc oxide and aluminium oxide in methanol synthesis originates from Dupont data summarized by Lücking (2017). As the quantity of water used for cooling the methanol synthesis system was also unavailable, a flow of seawater is assumed to enter at 20 ° C, reaching 25 ° C while cooling the system and being recycled with a 95% efficiency.

The LCA model is designed in OpenLCA software, due to its ease of use for scenario development and associated sensitivity analysis, its user-friendly contribution analysis options and the open-source nature. Finally, information on background processes comes from the ecoinvent 3.4 database, as it is considered “the largest, most consistent and most transparent database on the market” (Ecochain, 2019).

3.2.4 Flowcharts

The following section contains flowcharts of all alternatives examined, namely CO_2-methanol, fossil methanol and biomethanol. First, the full CO_2-methanol production process is presented (Figure 3.5), followed by a detailed overview of the DAC process, providing insights into a novel, in-depth DAC model (Figure 3.6). The CO_2-methanol alternative also considers a design variation. The main reason for this variation is that the DAC applied by Carbon Engineering takes advantage of natural gas to achieve the high temperatures required for calcination (see chapter 2). Since it is essential to move away from fossil fuels, yet the system kinetics need to be retained, an alternative design explored in this thesis uses biomass as a combustible. This is shown in Figure 3.7. Furthermore, flows of methanol from methane steam reforming and biomethanol are illustrated in Figures 3.8 and 3.9.

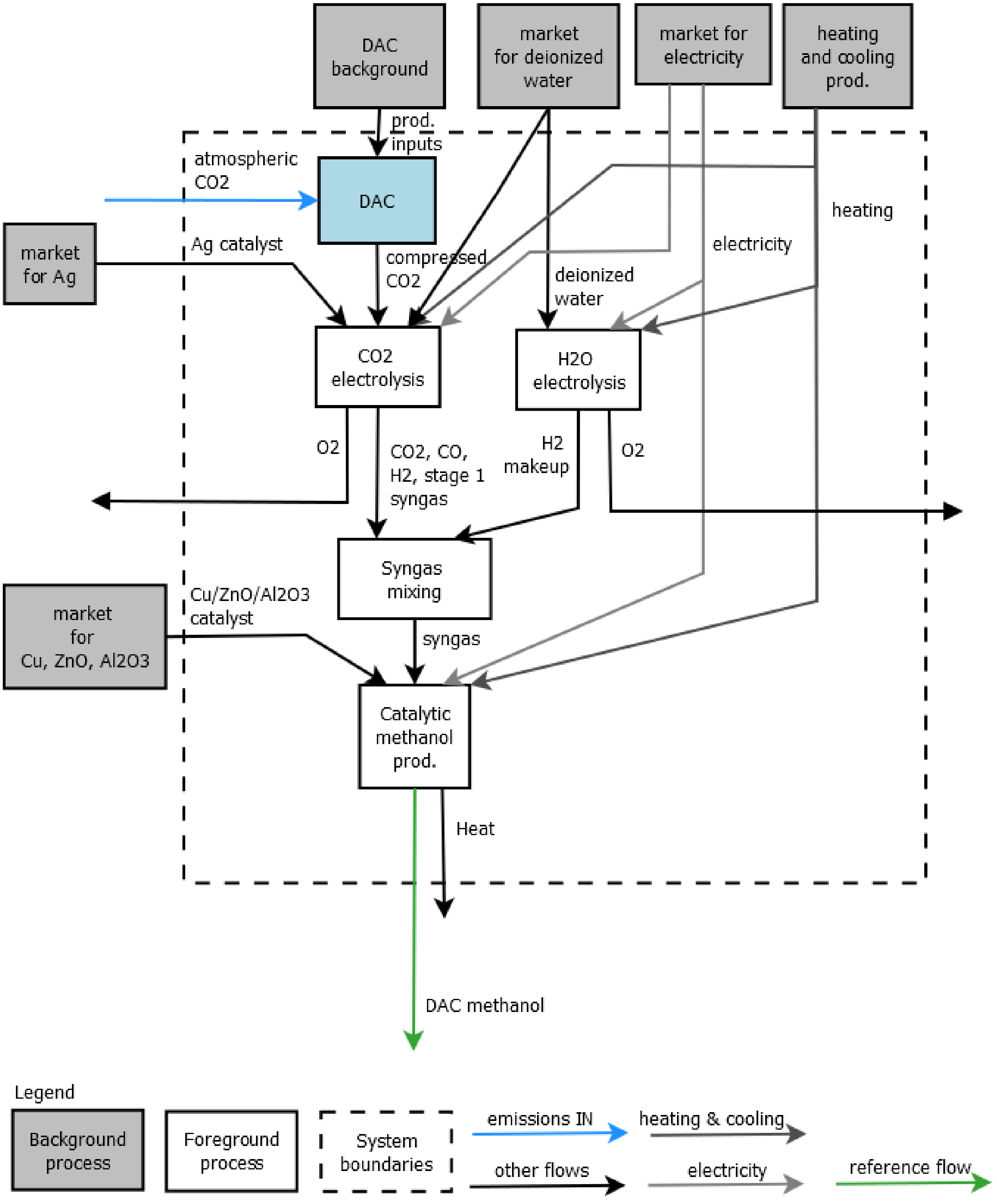


Figure 3.5: CO_2-methanol production

As shown in Figure 3.5, the first alternative produces methanol from CO_2 emissions by means of DAC. Some of the background processes include 'market' data, used in ecoinvent 3.4 to offer an average composition of a particular flow or process. The electricity from the market specifically provides wind electricity. It is assumed that the energy supply of this wind energy is continuous, having the intermittency of renewable energy sources resolved by a network. Additionally, as high-purity water is required for water electrolysis, a flow of deionized water is used in the model. The DAC process is highlighted in light blue colour, to reflect the higher level of detail used for modelling it. Below, figures 3.6 and 3.7 show all flows and processes modelled within the DAC.

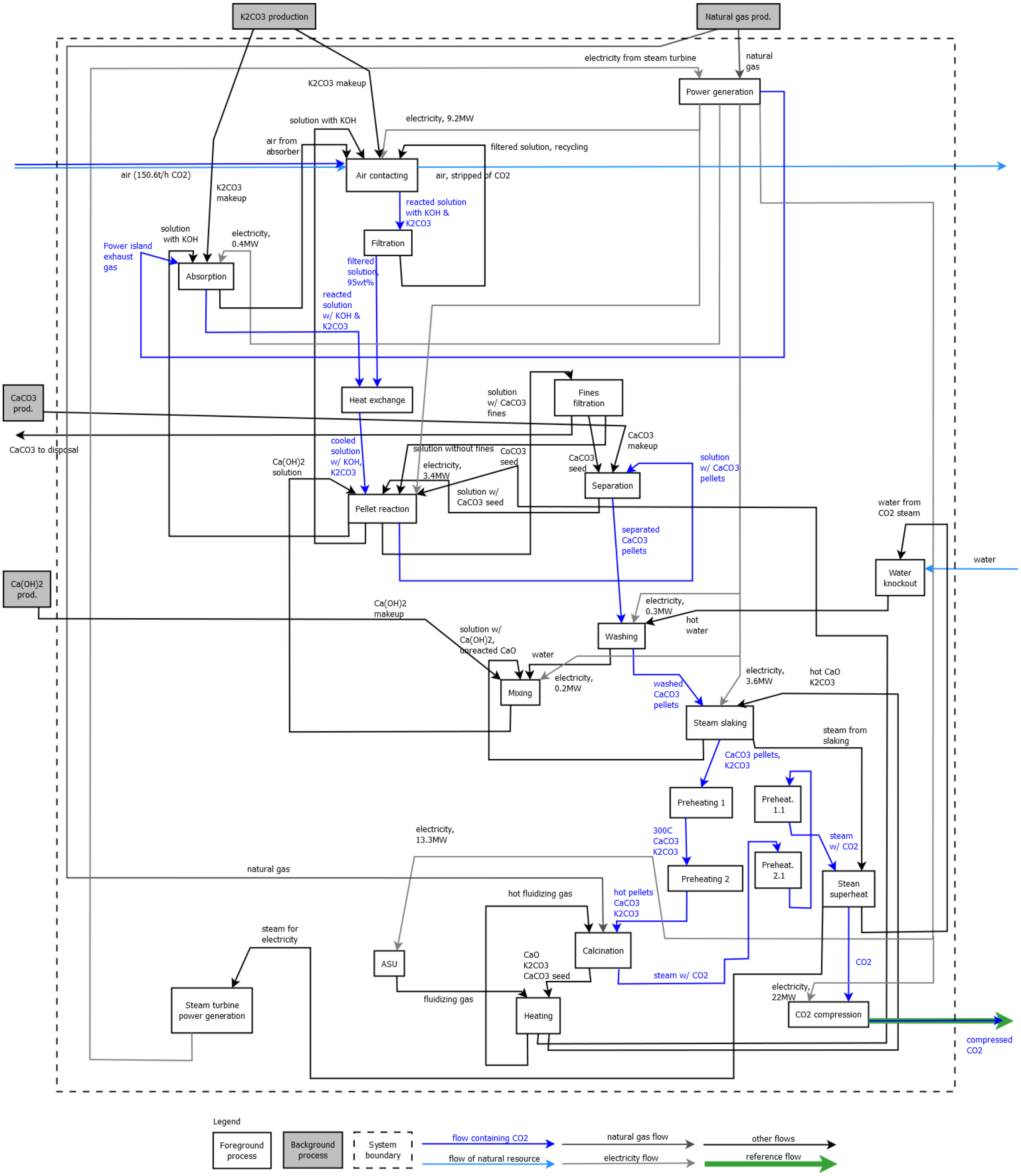


Figure 3.6: Direct air capture. Design based on the process of Carbon Engineering.

In order to reflect the industry practice of striving for the highest efficiency possible, the DAC model shown in Figure 3.6 contains a considerable number of flows, which are recirculated within the system and recycled. Furthermore, as chemical reactions take place in the process and change the flow composition without an additional need for external inputs, relatively few products from the background processes enter the system.

Additionally, it can be noted that Preheat 1 and Preheat 2 (shown in the bottom right corner of Figure 3.6) are split into two processes. This was done after consideration of various modelling practices, due to a linear nature of LCA, where it is assumed that flows of a process flow in one direction. More specifically, Preheat 1 and 2 heat up the pellets of calcium carbonate and simultaneously recirculate steam with released carbon dioxide. Nevertheless, from the modelling perspective, these two processes cannot be two-directional. This is why Preheat 1 and 2 in the model only take the role of pellet warming and 'dummy processes' called Preheat 1.1 and 2.1 recirculate the steam.

Figure 3.7 presents an almost identical process design. The one alteration present is the source of energy chosen. Unlike the natural gas flow used in Carbon Engineering's process, this alternative takes advantage of biomass to produce heat (brown arrow). It should be noted, however, the ecoinvent's levels of detail of biomass production compared to natural gas production are quite different, providing more comprehensive data on processes linked to the latter. Additionally, this background data does not recognize biomass' potential to absorb carbon dioxide, also known as biogenic carbon. Nevertheless, due to a lack of richer data source, ecoinvent's biomass production is used in the model.

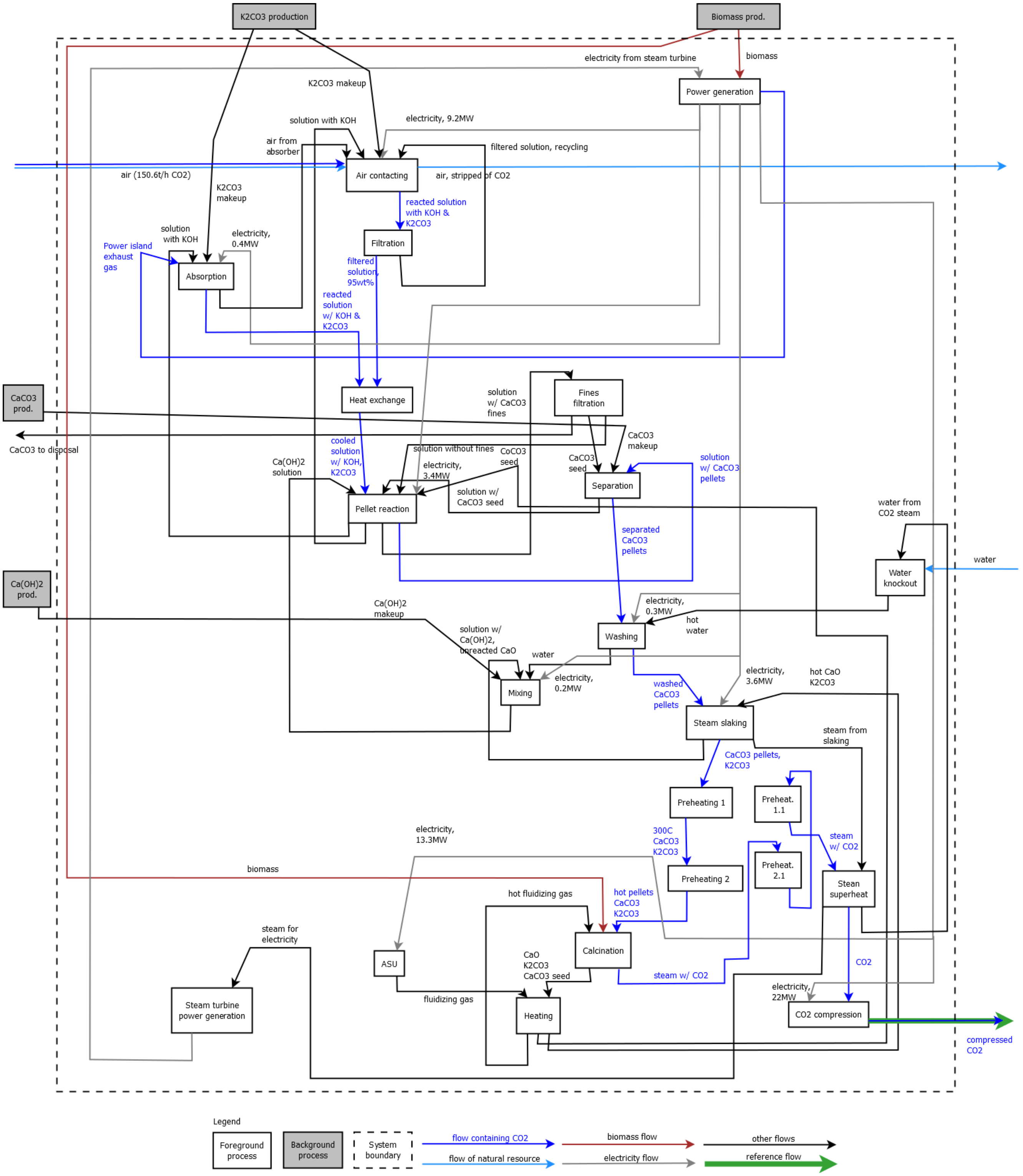


Figure 3.7: Direct air capture. Modified design of Carbon Engineering's process, using renewable energy from biomass.

As mentioned earlier, Figures 3.8 and 3.9 show the competitive alternatives to CO_2-methanol, namely methanol from natural gas reforming and biomethanol, respectively. LCA models for these two alternatives are adopted from ecoinvent 3.4 and are somewhat simplistic, as they reflect the fuel production from a black-box perspective. In other words, necessary inputs are taken from relevant markets and combined in one foreground process, which results in an outflow of fuel. Noteworthy is the presence of deionized water in both cases, as well as the input of wastewater in case of biomethanol. Moreover, the biomethanol model seems to lack the input of biomass, however, when inspecting the production of synthetic gas for biomethanol, it becomes clear that its source is wood. Similarly as in the biomass DAC system, the process is used within this LCA due to a lack of a more comprehensive alternative available.

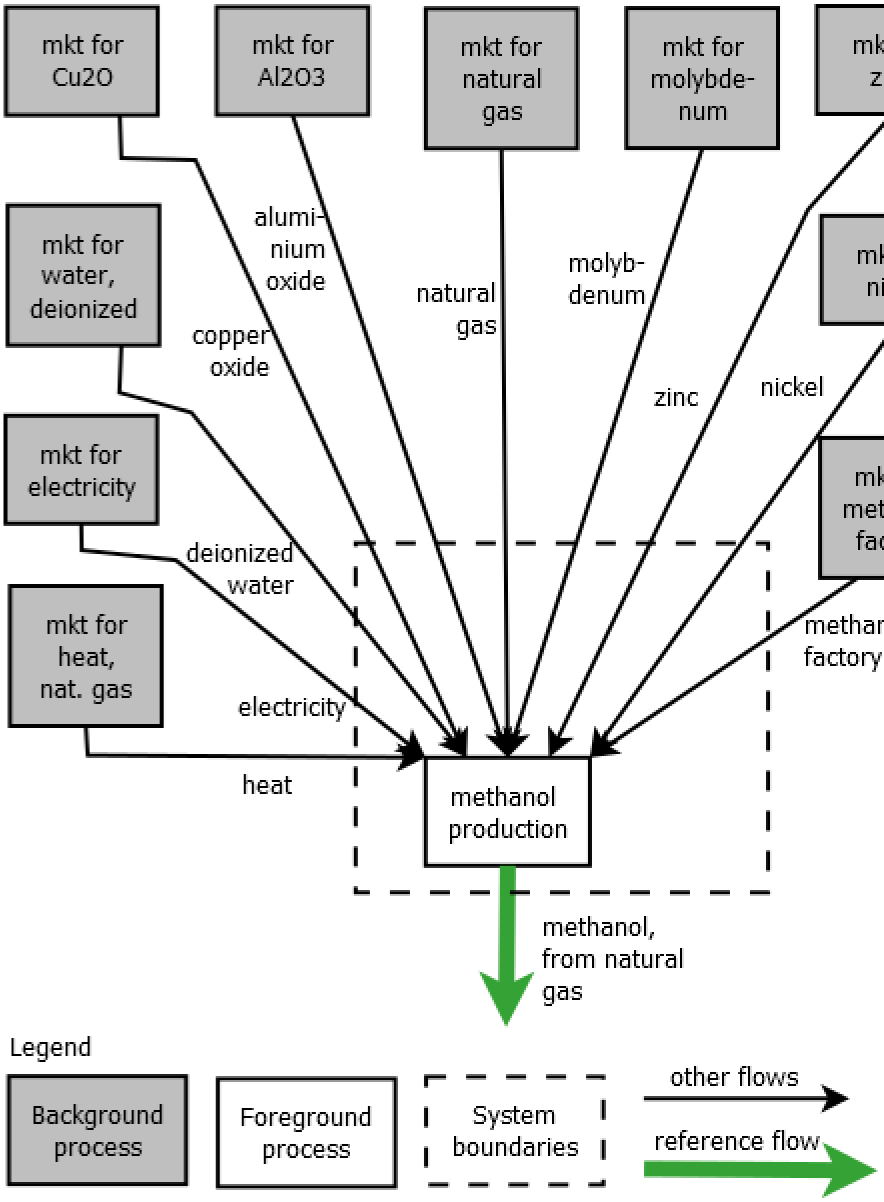


Figure 3.8: Methanol from natural gas steam reforming. Ecoinvent 3.4 background process UUID *4a0b47d3-c643-4b67-841b-b5689787f7a1*.

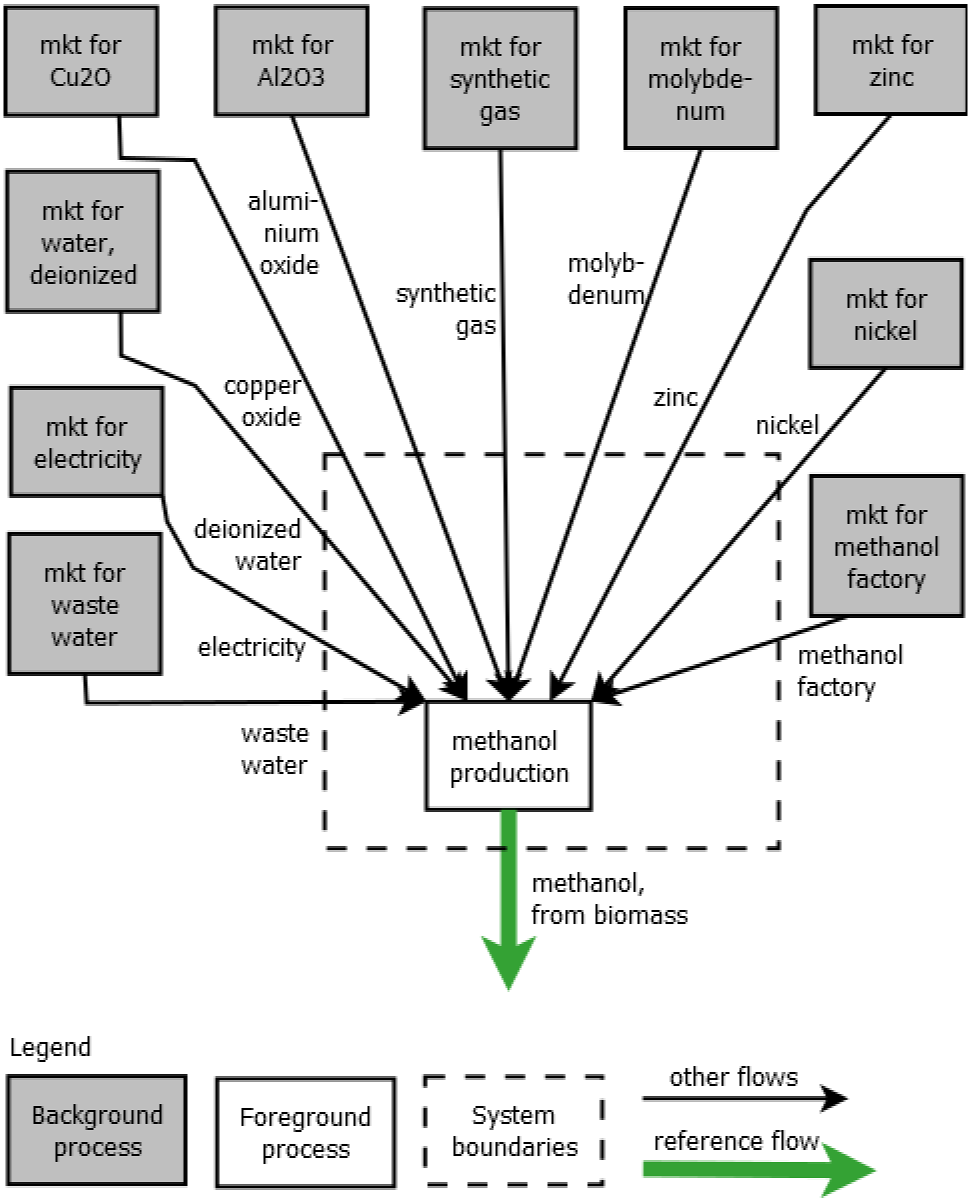


Figure 3.9: Biomethanol production. Ecoinvent 3.4 background process UUID *cd76f468-9b44-410f-a4e1-908b90e7bd81*.

3.2.5 Scenario building as means of sensitivity analysis

Building scenarios can facilitate projections on how anticipated events can affect development (Höjer et al., 2008). In this thesis, such projections are used for the sensitivity analysis, as the CO_2-methanol production is currently only deployed at a lab scale. The variables used in the scenarios are based on what is most likely to happen, reflecting a likely development if “ongoing trends continue in the future” (Höjer et al., 2008, pg. 1960). Additionally, the variables reflect intrinsic factors, i.e. those that are directly related to the technology itself and influence the life cycle inventory of the technology (Miller & Keoleian, 2015). The intrinsic factors are the following: efficiency and functionality change, spatial effects, infrastructure changes and resource criticality (Miller & Keoleian, 2015).

In order to create unified scenarios based on the variables described above, General Morphological Analysis (GMA) introduced by Ritchey (2011) is applied. GMA methodology allows for examining sets of possible future configurations by designing sets of scenarios with multiple variables. Such an approach leads to explorations of scenarios that are 'possible, viable, practical and interesting' (Ritchey, 2011). This methodology is only one of several possible scenario building approaches and to the author's knowledge, adoption of scenarios in LCA is still under development. GMA was particularly chosen as it allows to integrate multiple relevant, yet possibly unrelated parameters and to develop comprehensive scenarios.

The following section describes possible futures for two alternative scenarios and variables reflecting future development. These variables are summarized in Table 3.1, providing a quantitative representation of system alterations and an overview of how optimistic or how pessimistic these scenarios are. The overview is followed by short narratives of two scenarios applied.

The extent of system alterations per scenario

Table 3.1 below shows three scenarios – baseline, optimistic and pessimistic with corresponding parameters and their alterations. The parameters are categorized per subsystem. Note that while the optimistic scenario always counts with an improved performance in comparison to the baseline, the pessimistic scenario sometimes assumes that a parameter stays the same, as a certain efficiency has been achieved and reported and it is, therefore, unlikely that the process will perform worse. Most of the parameters come from the DAC system, as DAC is in the centre of attention of this thesis. Results of alteration of parameters within these scenarios are quantified and reported in Chapter 4.

Table 3.1: Three scenarios consisting of variables within each process of CO_2-methanol production based on most likely events, most interesting to explore. Quantified results of parameters per scenario are presented in Chapter 4.

	Parameter	Scenario		
		Optimistic	Baseline	Pessimistic
DAC	captured CO2	+10%	1	1
	solvent - KOH	-10%	1	+10%
	solvent - K2CO3	-10%	1	+10%
	heating req.	-10%	1	+10%
	CaCO3 makeup	-10%	1	+10%
CO2 el.	Ni contained in NiAg	+33%	1	-33%
	electricity req.	-5%	1	1
H2O el.	KOH electrolyte ratio	-50%	1	+67%
	electricity req.	-5%	1	1
CH3OH syn.	Cu/ZnO/Al2O3 ratio	-20%	1	1
	water recycling rate	+4%	1	-5%

Optimistic scenario

For the DAC process under the optimistic scenario, one of the possible futures that were considered models optimized air contacting, resulting in a higher carbon dioxide capture rate. In line with the higher rate of CO_2 capture, it is assumed that the need for natural gas input can be lowered to a certain extent, as a part of the reason to use natural gas seems to be the production of additional carbon dioxide (this is discussed in more detail in section 4.1.2). Additionally, as previous Carbon Engineering's system was based on NaOH solvent in place of potassium hydroxide, such alternative was also taken into account. However, it is not applied in this study, as it seems that the company chose KOH for the sake of better system dynamics. Instead, a lower KOH input is inspected. Furthermore, under this scenario, it is assumed that better process efficiency is achieved, leading amongst others, to lower quantities of calcium carbonate seed to disposal and consequently to a lower amount of $CaCO_3$ makeup.

When it comes to the CO_2 electrolysis, the optimistic scenario assumes that catalyst composition can change to exclude the usage of highly environmentally pollutant silver. Additionally, a better process efficiency leading to lower electricity requirements is examined. Regarding the water electrolysis, a reduced quantity of electrolyte is inspected, along with a lower electricity need. Finally, methanol synthesis under the optimistic scenario considers a higher recycling rate of water applied for cooling purposes and a lower usage of catalyst in the process.

Pessimistic scenario

Under the pessimistic scenario, one of the first futures considered is a need for a larger air capture unit. However, as Carbon Engineering is presently operating its DAC plant and achieves capture quantities reported, it seems unlikely that such an event would take place. Instead, we assume that no further optimization takes place and the system continues to capture the same amount of CO_2 as it does nowadays. With regards to the solvent used, it seems unlikely that a substance with even higher environmental impacts will be utilised. Instead, it is assumed that more solvent with the same level of emissions is used, i.e. KOH. Furthermore, we model a possibility of higher combustion rate of natural gas in the system, not only continuing the usage of fossil fuels, but amplifying it.

Within the CO_2 electrolysis process, the same quantity of catalyst is inspected, however, in an altered composition, utilizing a higher proportion of silver than in the baseline. The electricity requirement is assumed to stay equal to that of the baseline. This is also the case for water electrolysis. However, in the water electrolysis process, a higher electrolyte application is examined. Finally, the methanol synthesis is assumed to use the same amount of catalyst as in the baseline scenario, however, the recycling efficiency of cooling water is reduced by 5%.

3.3 Evaluation of LCA's suitability for assessment of DAC

The following section explains why our DAC LCA model uses composite flows and how modelling multiple recycling loops is treated in terms of allocation and process linking within the system. A part of the methods described was adopted in the model after the evaluation of the first results, as these results did not meet the expected values. This is in line with the iterative process explained at the beginning of this chapter.

3.3.1 Composite flow modelling

As the data provided by Keith et al. (2018) quantifies the liquid mass flows in terms of molar concentrations, the amounts of substances contained in each flow must be calculated before checking whether it is balanced, and subsequently modelling it in the OpenLCA software. Due to restricted access to the chemical engineering software 'Aspen', the composition of each mass flow was computed manually. After a lengthy process, detailed information on the DAC system was obtained, including quantitative data on changes in mass flow compositions due to chemical reactions. In order to preserve the richness of this data, the author decided to model the flows as multiple substances flowing in and multiple substances flowing out, even when they are a part of one mass flow.

A similar practice has been described by Clavreul, Baumeister, Christensen, & Damgaard (2014), who modelled waste flows in high detail, also demonstrating which materials were present in these flows. Although the author only discovered the work of Clavreul et al. (2014) after having modelled the system in a composite flow manner, the reasoning explained in their study is very closely in line with our logic behind modelling DAC in terms of elements within each flow. Namely, such approach allows for "keeping track off masses and substances", and for assessing the impact of various parameters, such as flow composition, on the environmental performance results (Clavreul et al., 2014).

3.3.2 Multiple recycling loops modelling

With the goal of building an LCA model that reflects the real-life industrial processes, the DAC model contains multiple recycling loops, as described in process engineering data published by Keith et al. (2018). Nevertheless, it is more common to build simplified models, which is why there are uncertainties among the scientific community regarding how the software deals with recycling loops.

As shortly mentioned above, the first examination of the results suggested a significant underestimation of environmental impacts of DAC. This is further explained in chapter 4 – Results. Still, efforts were made to understand the effect of recycling loops on the LCA results and the functioning of OpenLCA with regards to recycling. To deal with the results discrepancies, a simple model was designed by Carlos Blanco, where recycling loops were tested. Based on this, three hypotheses on how to model recycling loops in OpenLCA were developed. These hypotheses are as follows:

H1: all recycling flows need to match exactly. In other words, if a flow out contains 10 kg of mass that gets recycled, then two processes which it enters need to record an input of e.g. 8 kg and 2 kg of the product produced by the first process.

H2: the computational structure of LCA in processes that produce multiple outputs is based on allocating a proportion of impact to each of the outputs, for instance with regards to mass of each output, their economic value, energy content or other. For the system with multiple recycling loops to be calculated correctly, a custom allocation needs to be put in place and all products of one process need to have a total allocation of 1. In other words, if a process A has four products/by-products, then we can allocate their impacts, for example by 0.25 each. This is only valid if none of the by-products leaves the system.

H3: the reference flows need to be linked from the first process to the system reference flow. This is for the allocation to work properly. Even if the OpenLCA system diagram shows a linked system, this does not necessarily mean that it is linked from the first to the last process by reference flows. Instead, it is possible for the system to be linked also by flows of by-products. In such a case, the diagram appears correct, however, the allocation does not function as it should, and therefore, it needs to be corrected.

The DAC model was adjusted to meet all three hypotheses. Impacts of the adjustments on the inventory results and further examination strategy are explained in chapter 4 – Results. As the remaining parts of

CO_2-methanol production contain data of lower uncertainty than that of DAC, these subsystems are modelled in a more simplified way. Nevertheless, in reality, these processes are also optimized and take advantage of recycling flows and closed loops.

4. Results

This chapter lays out the results per research objective, presented in chapter 3. As the model was run twice and adapted after the first inventory results examination, the order of the objectives is slightly changed in this section. Namely, objectives two and three are reversed. Therefore, the DAC data analysis is followed by an evaluation of LCA suitability and finally, LCA results of the alternatives presented in chapter 3 are discussed. This shift in the objective order reflects the iteration within the research conducted.

4.1 Data analysis of DAC – level 2

Figure 4.1 shows the overview of processes within the Carbon Engineering's DAC system. The four main parts of the system, namely the air contactor, pellet reactor, calciner and slaker, are shown in light green colour. Each of these parts is briefly introduced below, reflecting on relevant reactions, which were introduced in chapter 3.1 and are presented per process again in the below section.

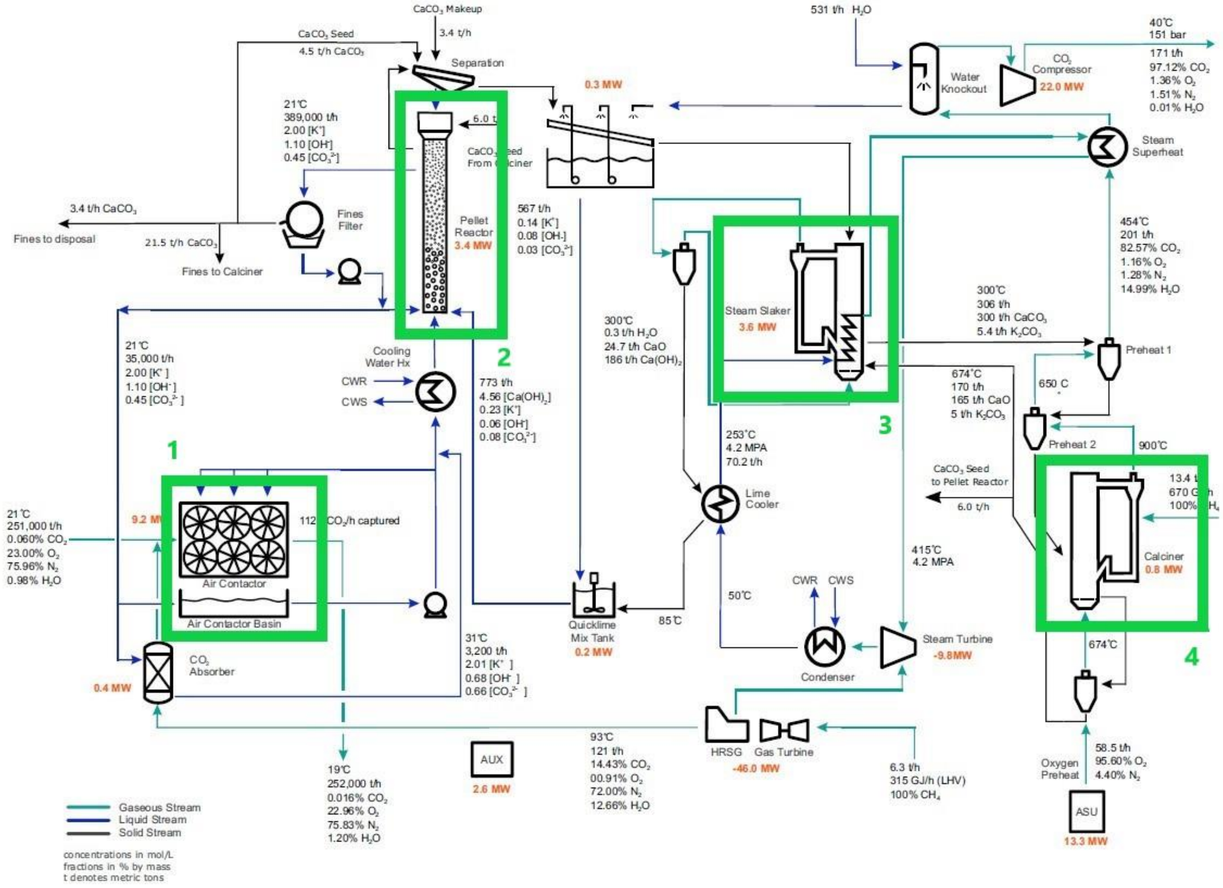


Figure 4.1: DAC system and its four main components. Adapted from Keith et al. (2018)

4.1.1. Overview of main processes

Air contactor

Shown in the bottom left corner, the air contactor based on cooling tower technology captures a stream of air containing carbon dioxide. Then, this flow of air is blown onto a thin film of the liquid solvent containing potassium hydroxide. Potassium hydroxide reacts with carbon dioxide and binds it in the form of potassium carbonate. Potassium carbonate present in the reacted liquid solvent then gets filtered and cooled, after which it enters the pellet reactor. This is summarized in Equation 1:

Equation 1: binding of carbon dioxide into liquid solvent

$$CO_2 + KOH \rightarrow H_2O + K_2CO_3$$

Pellet reactor

Indicated by number 2 in the upper left part of Figure 4.1, the pellet reactor receives the liquid solvent with potassium carbonate from the air contactor and calcium hydroxide from the quick lime mix tank. These streams then react to produce pellets of calcium carbonate (Equation 2). The pellets 'grow' within the reactor and thanks to the presence of a fluidizing bed, they are lifted towards the upper part of it once they achieve a specific size. Then, they are separated, washed and sent to the slaker. The smaller particles of calcium carbonate present in the liquid solvent are circulated through a filter. While most of the flow re-enters the pellet reactor, a small portion of calcium carbonate fines are disposed of.

Equation 2: calcium carbonate pellet production

$$K_2CO_3 + Ca(OH)_2 \rightarrow 2KOH + CaCO_3$$

Steam slaker

As indicated in its name, the main purpose of the steam slaker (number 3 in Figure 4.1) is to generate steam for the steam turbine. Although the steam slaker receives the calcium carbonate pellets, it does not process them, only passes them on to the calciner. Instead, the steam slaker receives calcium oxide from the calciner, which reacts with water, and produces calcium hydroxide (Equation 3) necessary for the pellet reactor.

Equation 3: calcination and carbon dioxide release

$$CaCO_3 \rightarrow CaO + CO_2$$

Calciner

The right bottom corner of Figure 4.1 illustrates the calciner. Here, the pellets of calcium carbonate get exposed to high temperatures and dissolve into calcium oxide and carbon dioxide (Equation 4). From the perspective of DAC regeneration methods, discussed in the system background, this is temperature swing adsorption, in this case, applied by natural gas combustion. The resulting calcium oxide enters the slaker, as explained above, and the released CO_2 gets compressed in the compressor.

Equation 4: slaking - quick lime production

$$CaO + H_2O \rightarrow Ca(OH)_2$$

4.1.2. Data analysis and the balancing of the system by Keith et al. (2018)

This section discusses discrepancies identified in the article published by Keith et al. (2018), ranging from mistakes in the graphical representation of the flows (direction or state) to unbalanced material flows and the reasons for natural gas usage in the system. There were no issues identified in the energy flows within the system, as flows indicated were balanced. To model the DAC flows, which needed corrections, additional or excess proportion of the flows calculated came from background processes from the ecoinvent3.4.

Pellet reactor

Starting with minor issues in the processes around the pellet reactor, one can observe that a flow of 35,000 t/h KOH solvent flows in two opposite directions – from pellet reactor to air contactor and back, where it is also joined by a flow of filtered solution from fines filter. While these errors did not require the balancing of the mass flows, in the data for the LCA model, it is assumed that the KOH solvent only flows from the pellet reactor to the air contactor, and that the filtered fraction enters the pellet reactor rather than the flow of the KOH solvent.

Additionally, there is a liquid flow entering the pellet reactor from a separation unit, even though no aqueous flow entered this separation unit. For the modelling purposes, we assume that the flow from the pellet reactor to the separation unit also contains a stream of water, which then becomes the source of liquid flowing out of the separation unit. This flow is otherwise categorized as a solid flow and contains the calcium carbonate pellets along with calcium carbonate fines.

Moreover, a flow of 'fines to calciner' from fines filter does not enter the calciner itself. This is, however, already discussed by Keith et al. (2018), who claim that disregarding the second half of the issue leads to a simpler, easier to work with, model.

A more significant issue was identified in the mass of the flow from the pellet reactor to the fines filter. Namely, a flow containing 389,000 t/h leaves the reactor, even though the content that enters the reactor is less than 9% of this quantity. More specifically, the pellet reactor receives 33,468 t/h from the heat exchanger, 777.7 t/h from mixing and 6 t/h from heating from the slaker. Due to this large discrepancy in flows in and out equivalent to more than one order of magnitude, it was concluded that this issue could have been a typing error. In the model itself, this flow was kept as reported, however, it is assumed that it keeps on being completely recirculated without a need for an additional input of water from the environment.

Quick lime mix tank

Although only mentioned briefly in the process overview, some of the major inaccuracies identified originate from the quick lime mix tank. The main inaccuracy is in the mass of calcium hydroxide flow, essential for the production of calcium carbonate pellets. As can be seen in the centre of Figure 4.1, 186t/h of calcium hydroxide leaves the slaker and enters quick lime mix tank. After getting mixed with water from pellet washing, a flow of 773 t/h, containing 262.79 t/h of calcium hydroxide enters the pellet reactor. It is unfeasible for calcium hydroxide to increase its volume by 76.79 t/h via dilution with water, simply because a stream of water does not contain calcium hydroxide.

Nevertheless, the slaker output value of 186 t/h seems to be correct, as it is consistent with the authors' claim that 85% of calcium oxide present reacts to produce calcium hydroxide. In other words, out of 164.5 t/h calcium oxide given, 139.8 t/h is needed to produce 186 t/h of calcium hydroxide, equal to 85%. To preserve consistency, an inflow of virgin calcium hydroxide corresponding to 76.79 t/h is added in the model. Additionally, 76.79 t/h of water to mixing are subtracted, as the initial total mass of the flows appears to be correct. This way, the mass balances from the slaker, through quick lime mix tank, to the pellet reactor are resolved.

However, only a partial flow of calcium hydroxide is needed to produce 300 t/h of calcium carbonate pellets. This raises a question about what happens with the unreacted amount of calcium hydroxide, equal to 29.23 t/h. A simple answer could be that the actual yield of the reaction is 88.88%, although it remains unclear whether the remaining reactant accumulates within the pellet reactor, is separated and reused, or becomes a waste. Due to this unclarity, in the model, we assume that the entire flow gets consumed.

Similarly, 24.7 t/h of unreacted calcium oxide flows into the quick lime mix tank and it is not clear whether this mass continues to the pellet reactor and through separation process back to the slaker. For the modelling purposes, it is assumed that this quantity does not leave the system, nor does it require additional output from the background processes.

Steam slaker

As shown in the upper right part of Figure 4.1, a flow containing 5.4t/h of potassium carbonate (K_2CO_3) leaves the slaker and enters the calciner. Afterwards, 5t/h of this substance leaves the calciner and re-enters the slaker. For the sake of mass balances, it is assumed that the value from the calciner to the slaker is also equal to 5.4 t/h. Nonetheless, it is uncertain why potassium carbonate is recirculated back and forth between the two parts of the system.

Water knockout

Another issue is identified in the upper right part of Figure 4.1. More specifically, the chart suggests that a flow of steam that leaves steam superheat and contains released carbon dioxide, enters the water knock-out, where it would meet a flow of water. This is undesirable, as it would increase the water content of the CO_2 to the compressor, potentially leading to corrosion of the equipment.

In line with this, it seems unlikely that that flow from water knock-out enters the CO_2 compressor. Instead, the model developed for this thesis assumes that the flow from steam superheat enters directly to the compressor and leftover hot steam enters the water knockout, where it heats up the water to the quick lime mix tank.

Natural gas usage

When cross-examining the balance of carbon dioxide, it becomes clear that out of 166.08 t/h captured, 54.08 t/h must come from within the system, most likely from natural gas. Even though the authors openly declare capturing emissions created when burning natural gas for energy purposes, such emission levels normally range between 4% and 7%. This would supply the system with an additional inflow of carbon dioxide of between 0.79 t/h and 1.38 t/h, respectively, from both the calciner and the power island, nowhere close to the missing 54.08 t/h. Even if we consider a 14% concentration, as indicated by the authors, this would yield only 2.76 t/h of carbon dioxide.

Equation 5: Natural gas combustion.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Based on Equation 5, it is possible to produce the missing quantity of CO_2. Namely, 17.46 t/h of CO_2, suggested by Keith et al. (2018) in Figure 4.1 (14.43% of 121 t/h flow) can be produced from natural gas input to the power island. Likewise, 13.4 t/h of methane input to the calciner can lead to the production of 36.62 t/h of carbon dioxide. The authors already disclaim the production of oxygen, sufficient for such a reaction to take place. Nevertheless, this suggests that the usage of natural gas has been chosen for purposes other than the heating requirements. Additionally, it implies that the technology is built around the combustion of natural gas and its kinetics potentially cannot be implemented without fossil fuels (or biomass). Therefore, it is questionable what role proposed DAC would have in decoupling from fossil fuels, as it promotes their continued use.

4.2 Data analysis of DAC methanol – level 1

4.2.1 Summary of the main processes

As the overview of technology applied in DAC methanol production is already given in the system background, this section only provides a brief summary of reactions within the remaining processes leading to the production of DAC methanol.

First, a flow of compressed carbon dioxide from DAC enters the CO_2 electrolyser, along with a flow of deionized water and electricity. In this way, synthetic gas is produced. However, as the composition of this syngas is not favourable for catalytic conversion to methanol due to a relatively low quantity of hydrogen present, an additional hydrogen quantity is produced by the means of H_2O electrolysis. H_2O electrolysis uses an input of deionized water, along with electricity and leads to an output of high-purity level hydrogen. The two streams produced by electrolyses are then mixed, after which a thermo-catalytic conversion to methanol takes place.

4.2.2 Data analysis and balancing of the system by Torri (2019)

As mentioned in the methodology, data provided by Torri was of lower uncertainty, and an inspection of reported flows into the system and out of it showed that the mass and energy flows were already balanced. This analysis represents the level 1 assessment of data. The only missing values needed for the modelling purposes were the quantities of catalysts used, their composition, and the recycling rate of cooling water needed for the thermo-catalytic conversion process. Table 4.1 below gives an overview of energy flows and Table 4.2 summarizes the mass flows from and to the background of our system.

Table 4.1: Energy balance of DAC methanol system. Note that energy flows of DAC represent an annual production of 1.46 Mt of compressed CO_2, while the DAC methanol production only requires 27.4 kt/year of CO_2.

Subsystem	Stream	Unit	Input	Output
DAC	Input from natural gas	GJ/y	8.81	-
	Heating and electricity consumption	GJ/y	-	8.81
CO2 electrolysis	Electricity input, from wind	TJ/y	642.3	
	Electricity consumption	TJ/y	-	642.3
H2O electrolysis	Electricity input, from wind	TJ/y	226.96	-
	Electricity consumption	TJ/y	-	226.96
Catalytic synthesis	Electricity, from wind	TJ/y	17.75	-
	Cooling, from sea water	TJ/y	139	-
	Heat produced by waste incineration	TJ/y	-	13
	Energy consumption	TJ/y	-	143.75

*Table 4.2: Mass flows within the DAC methanol system. * - balancing flows, where inaccuracies in reported data were identified, ** NG input used for both CO_2 production and as a source of energy, *** - fraction of all water needed for cooling, corresponding to non-recycled part of the flow. DAC mass flows reflect an annual production of 1.46 Mt CO_2, remaining processes utilise 27.4 kt.*

Subsystem	Stream	Unit	Input	Output
DAC	CaCO3 makeup	kt/y	29.8	-
	CO2 captured from the air	Mt/y	1.0	-
	K2CO3 makeup*	kt/y	30.5	-
	KOH solvent*	kt/y	112.6	-
	Natural gas**	km3/y	0.2	-
	CO2 from natural gas	Mt/y	0.5	-
	Disposed CaCO3 fines	kt/y	-	29.8
	Compressed CO2	Mt/y	-	1.5
CO2 electrolysis	Compressed CO2	kt/y	27.4	-
	Deionized water	kt/y	2.0	-
	Ni catalyst	kg/y	115.8	-
	Ag catalyst	kg/y	38.6	-
	O2 produced	kt/y	-	8.7
	Syngas 1	kt/y	-	15.4
H2O electrolysis	H2O feed	kt/y	21.2	-
	KOH electrolyte	t/y	3.6	-
	H2 produced	kt/y	-	2.4
	O2 produced	kt/y	-	16.2
Catalytic synthesis	Sygas, final composition	kt/y	17.8	-
	Water for cooling***	Mt/y	0.3	-
	Al2O3 catalyst	kg/y	51.8	-
	Cu catalysti	kg/y	83.5	-
	ZnO catalyst	kg/y	31.7	-
	Methanol produced	kt/y	-	16.7
	Boiler flue stream	kt/y	-	9.0

Having compiled this data on system inputs and outputs allowed for the construction of an LCA model. Nonetheless, as briefly mentioned above, the LCA model resulted in seemingly underestimated DAC results. The following section discusses this issue in more detail**.**

4.2 Suitability of LCA for assessment of DAC

When inspecting the inventory results of the DAC system, the author discovered that the OpenLCA software only recognizes the capture of approximately 6.28 t/h of carbon dioxide, far off the 112 t/h indicated by Keith et al. (2018) and also used as an input in the model. Therefore, it became clear that the model was not working as it should. The following section explains how the methodology was implemented to model the assessed system using LCA in this thesis and what steps were taken to tackle issues when they arose.

First, the application of composite flow modelling and multiple recycling loops are discussed. Then, issues observed in the later results are evaluated. Since it is not clear whether the issues in the later results originate from composite flow modelling, from multiple recycling loops, or a combination of the two, the evaluation of these results does not distinguish which modelling approach is responsible for which proportion of the issue.

4.2.1 Composite flow modelling

As mentioned in the methodology, DAC flows were modelled to show each substance within the flow. For instance, a flow of liquid solvent of potassium hydroxide, that leaves the air contactor and thus also contains carbon dioxide in form of potassium carbonate, is modelled as three different sub-flows, namely the mass of potassium hydroxide, the mass of potassium carbonate and mass of water. This approach was put in practice for the entire DAC system, in line with two-level data analysis applied.

The author was unaware that OpenLCA does not serve for this type of modelling and only discovered so after reading the study of Clavreul et al. (2014), who report unavailability of a software or an add-on for LCA of heterogeneous reference flows. Instead, it is a common practice to simplify the modelling and aggregate the flows or processes to a certain extent.

Unlike the DAC sub-system, the flows within the electrolyses and catalytic synthesis of methanol were modelled in a standard manner, in line with level 1 data analysis.

4.2.2 Multiple recycling loops modelling

As the DAC model was built to closely reflect the industry production practices, many recycling loops were modelled. According to *The computational structure of life cycle assessment* (Heijungs & Sun, 2002), recycling represents a situation where a product with a negative value gets transformed in a unit process to a product with a positive value. Therefore, it is an example of multi-functionality. Unlike standard multifunctional processes, closed-loop recycling, where an entire flow of secondary material gets reused within the product system, is an exception which creates an over-determined system by assigning an additional function to one of the processes (Heijungs & Sun, 2002). This translates into an occurrence of a rectangular matrix, which prevents the system from being calculated (or which causes it to be calculated incorrectly, based on the software used).

Since the closed-loop recycling avoids the use of virgin materials, the need to allocate is also avoided. Nevertheless, Heijungs & Sun (2002) propose implementing arbitrary allocation factors, which must add up to 100%, and this way, creating a 'pseudoinverse matrix'. This approach is the basis of hypothesis H_2, presented in Methodology.

In line with the methodology, three hypotheses were developed to tackle underestimated inventory results. All these hypotheses were applied to the model. First, all the recycled fractions were added up to ensure that they are equal to 100% of their original flow in terms of mass or energy. This was also checked by two other researchers, namely Mathieu Delpierre MSc. and Carlos Blanco MSc.

Second, a custom allocation method was applied to these flows, using the 'Economic allocation' in OpenLCA, assigning the flows an arbitrary allocation factor equal to a fraction of 100%. In other words, if air contacting leads to three outflows of goods – the mass of KOH, the mass of K_2CO_3 and mass of water, as explained above – then these flows are allocated on 0.3, 0.4 and 0.3 basis, respectively. The allocation factors within one process are always equal to one. Before running the model, 'Allocation – As specified per process' is selected.

Third, the sequence of process reference flows was examined by inspecting the order of products in and out. In other words, taking the system reference flow – namely compressed CO_2 – and clicking through each product in should lead to the first process within the DAC, specifically the air contacting. This way, it became clear that not all the processes from air contacting to carbon dioxide compression were linked via process reference flows. Therefore, the reference flows were artificially changed where needed to ensure a fluent chain of processes.

4.2.3 Results after implementation of alternative methods

After adopting the three hypotheses on multiple recycling loops, the inventory results were still not showing the capture of 112t/h CO_2. The author also attempted modelling the DAC system in different software, more specifically in CMLCA. This was done in two ways – first, following the composite modelling choice as well as multiple loop recycling, and second, aggregating the substances within each flow into one flow, as done regularly with multiple closed loops still present. Neither of the trials led to inventory results resembling the system inputs.

However, it was noted that after the adjustments, the inventory results in OpenLCA were between 20-25% of the environmental impacts compared to the impacts connected to the system using the same quantities of the same inputs, without recycling and without composite flows. This led to a theory that due to the multiple recycling loops, the system was experiencing a so-called 'mirroring effect'. To explain the mirroring effect, it is possible that as OpenLCA recognizes the recycled part of the flow entering a process, it determines that fewer resources are needed to produce required quantities of a product. Less product is made as fewer resources enter the process. But the mirroring effect persists, and so the quantities required get smaller and smaller. This is illustrated in Figure 4.2.

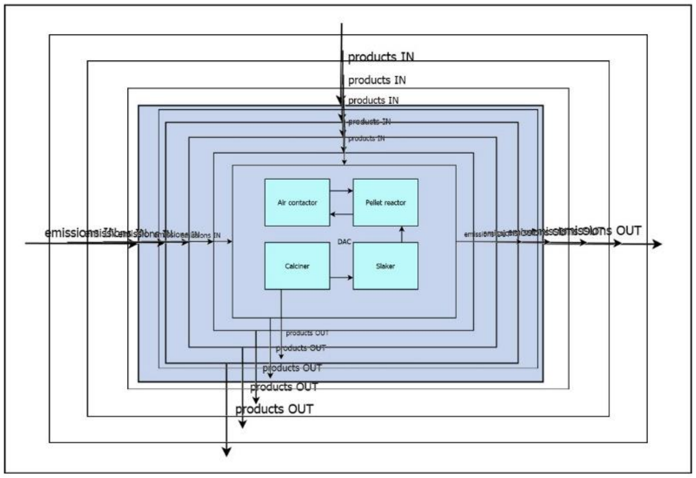


Figure 4.2: Mirroring effect in DAC LCA model, resulting in a significantly underestimated inventory results.

To prevent an underestimation of the climate change potential of the DAC system and to fully understand its environmental impacts, the results of the entire CO_2-methanol production LCA are shown in a black-box approach. This approach is built on cross-checked data, as an aggregated process with inputs and outputs, but without the sub-processes, recycling loops or composite flows. The modelling approach adopted suggests that the current state of LCA software is not sufficient for in-depth modelling representative of real-life industrial processes.

4.3 Life cycle assessment

The following section presents the LCA results of alternatives:

- 1a – production of 16.7 kt/year of CO_2-methanol with DAC based on Keith et al. (2018),
- 1b – production of 16.7 kt/year of CO_2-methanol with adjusted DAC system, utilizing biomass instead of natural gas,
- 2 – production of 16.7 kt/year of biomethanol,
- 3 – production of 16.7 kt/year of methanol from natural gas steam reforming.

Full inventory results are provided in Appendix B.

The LCA results are based on ILCD 2011, midpoint impact assessment method. The impact categories chosen are climate change, freshwater ecotoxicity, human toxicity (carcinogenics), human toxicity (non-carcinogenics), land use, resource depletion (mineral, fossils, and renewables), and resource depletion (water). Each of the impact categories is analysed below. This is followed by an in-depth contribution analysis of alternative 1a and sensitivity analysis based on optimistic and pessimistic scenarios.

4.3.1 Climate change

As can be observed in Figure 4.3, characterization results suggest that of the alternatives examined, CO_2-methanol production performs the best in terms of climate change impacts. Its production leads to climate change mitigation, especially when implementing DAC based on biomass combustion. What is surprising in these results, however, is that biomethanol records the worst environmental impact of the alternatives examined.

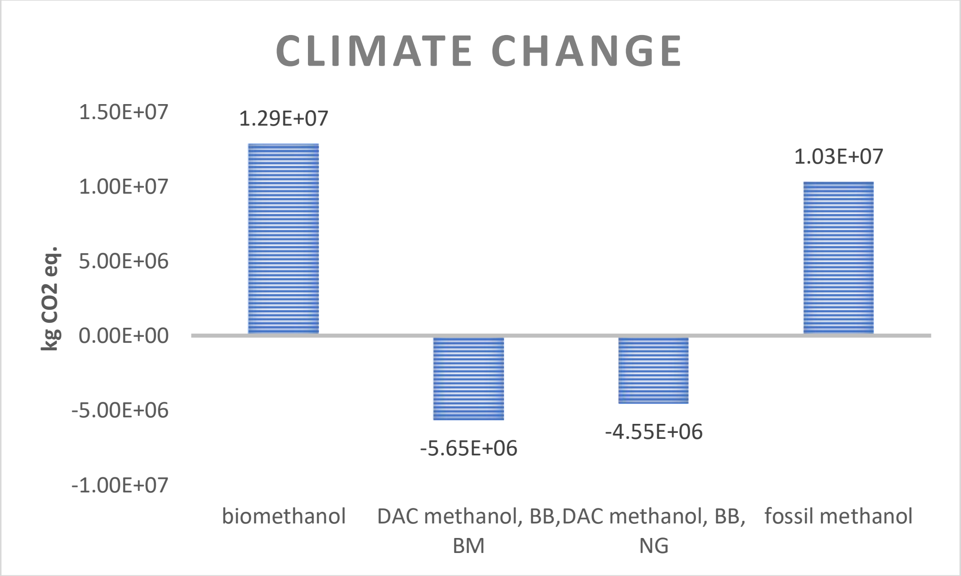


Figure 4.3: Characterization results of 4 alternatives for climate change, all producing 16.7kt/year of methanol.

When it comes to the source of impact per alternative, biomethanol records circa 98% of its impacts, equal to 1.3E+07 kg CO_2eq., from methanol production from biomass. This suggests that the processing of syngas pollutes to an extent larger than the negative emissions captured in the syngas, which is based on wood and captures -3.7E+07 kg CO_2eq. However, when summing these two contributions, it becomes clear that biomethanol should instead have a negative impact on climate change. Resulting negative impact would be equal to -2.4E+07 kg CO_2eq. This discrepancy in process contributions and rather unexpected large total impact indicate inconsistencies in biomethanol data in ecoinvent3.4 or its incorrect processing by OpenLCA, as the production of biomethanol is purely based on a background process from the ecoinvent database. This is further discussed in chapter 5.2.6.

Second, emissions from fossil methanol mostly originate from heat requirements from natural gas, responsible for 49% of the impacts, and input of high-pressure natural gas, equivalent to 37% of the impacts.

Third, in cases of DAC methanol from NG and BM, both options incur the most impact from the production of potassium hydroxide (3.9E+06 kg CO_2eq. in both cases), electricity from wind (3.4E+06 and 3.2E+06 kg CO_2eq., respectively) and potassium carbonate (1.3E+06 kg CO_2eq. in both cases). These emissions, however, are largely offset by the capture of carbon dioxide, leading to a negative total impact on climate change up to the well point.

4.3.2 Land use

An overview of land use results is provided in Figure 4.4. The most impactful fuel alternative when it comes to land use is biomethanol. This seems logical, as its production is based on syngas from wood, which requires land to grow. In line with this argument, 98% of all impacts come from syngas production.

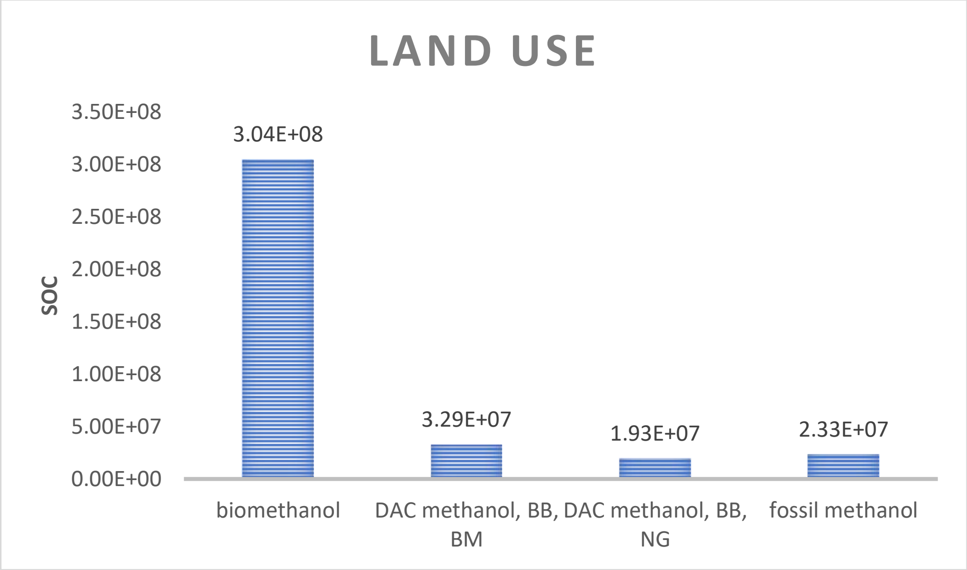


Figure 4.4: Characterization results of 4 alternatives for land use, all producing 16.7kt/year of methanol.

Inspecting the other fuel alternatives, DAC methanol NG performs the best and occupies less land that the fossil methanol alternative. Looking into contributions of land use burdens, 30% of impacts of DAC methanol NG, equal to 5.9E+06 kg SOC, comes from natural gas. This is followed by 30% from electricity and 26% from potassium hydroxide production, utilised for carbon dioxide capture.

DAC methanol BM contributes to the same extent of land use from potassium hydroxide production as its natural gas counterpart, equal to 5.1E+06 kg SOC. However, the biomass alternative uses almost double the land for electricity production, i.e. 2.5E+07 kg SOC. The rather high impacts linked to the electricity production can most likely be ascribed to the source of biomass used, namely torrefied biomass. This flow in was selected due to the absence of other economic sources of biomass, and unlike most ecoinvent products, it contains rather scarce data and only one source of environmental impact. Its pre-processing via torrefaction was deducted from the high lower heating value of 14.7MJ/kg.

Finally, most land use impacts from fossil methanol can be attributed to natural gas, namely 1.7E+07 kg SOC, corresponding to 75% and to heat production from natural gas equal to 3.4E+06 kg SOC or 15% of all impacts.

4.3.3 Resource depletion – mineral, fossils, and renewables

Figure 4.5 shows characterization results for resource depletion – mineral, fossils, and renewables. The environmental performance of CO_2-methanol in this impact category is the worst of the four alternatives researched. Although the impact on resource depletion of DAC methanol NG is almost 53% higher than that of DAC methanol BM, process contributions of these two alternatives are very similar. More specifically, electricity production from wind sources affects the results the most. In the CO_2 electrolysis it accounts for 62% (NG alternative) and 55% (BM alternative), followed by electricity for water electrolysis with 22% (NG) and 19% (BM). Another significant contributor to resource depletion is potassium hydroxide, accounting for 8% (NG) and 11% (BM).

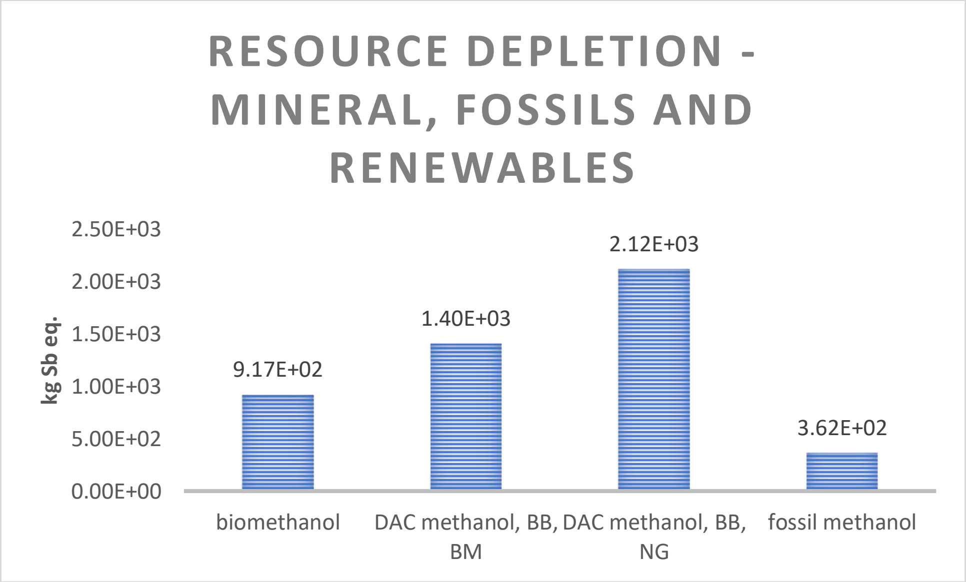


Figure 4.5: Characterization results of 4 alternatives for resource depletion - mineral, fossils, and renewables, based on an annual production of 16.7kt of methanol.

Hotspots of biomethanol manufacture lie in synthetic gas production (62%), methanol factory production (17%) and zinc production (13%). Although fossil methanol production is the most efficient of the four alternatives considering the resource depletion, it uses the same quantity of zinc as biomethanol, leading to depletion of 119.2 kg Sb eq. This is equal to 33% of resource depletion of fossil methanol production. The main impact of this alternative comes from methanol factory production (43%). Additionally, natural gas input contributes to 9% of the impact.

4.3.4 Resource depletion – water

As shown in Figure 4.6, most water is consumed by biomethanol. This is closely related to land use and requirements to grow the biomass. On the other hand, both options on CO_2-methanol production result in a very similar impact on water depletion, followed by fossil methanol production, which is most efficient in this aspect.

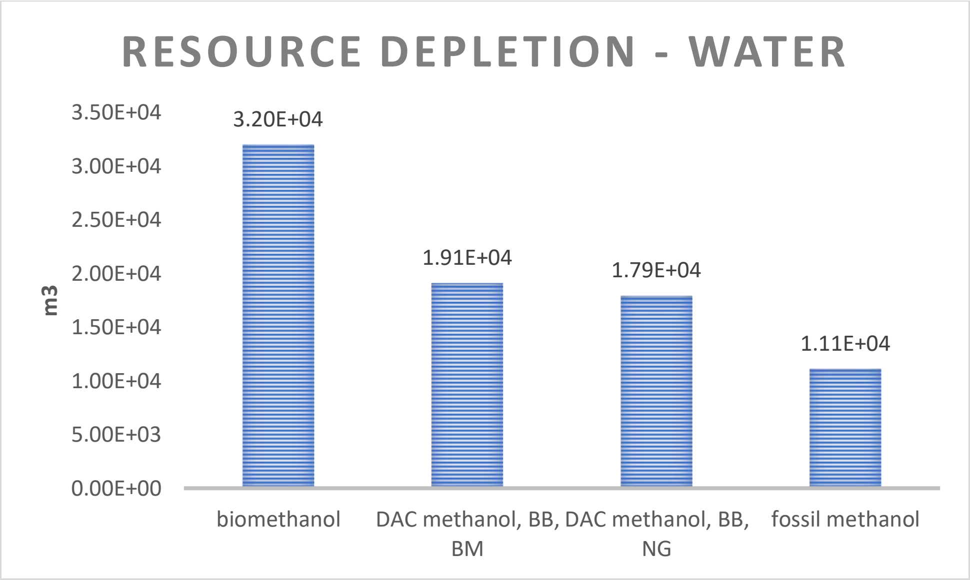


Figure 4.6: Characterization results of 4 alternatives for resource depletion - water, based on an annual production of 16.7kt of methanol.

Similar to resource depletion – mineral, fossils, and renewables, two DAC methanol options again record the most impacts in the same processes, namely electricity for CO_2 electrolysis (30% NG and 38% BM), potassium hydroxide production (25% NG and 24% BM) and deionized water input for H_2O electrolysis (18% NG and 17% BM). As the only difference between these alternatives is the input of natural gas or biomass, the impacts coming from KOH production and deionized water are identical, namely 4552.7 m^3 and 3205.6 m^3. Nevertheless, DAC using biomass has somewhat higher impacts related to electricity usage, likely due to the torrefaction process, as explained above.

Inspecting the contributions to fossil methanol impacts led to an interesting observation that the OpenLCA results do not show where 60% of the environmental burdens come from. It is unclear whether this is due to the data completeness from ecoinvent3.4 or the way that the software processes this data. This is further discussed in chapter 5.2.6. Nevertheless, the main known contributors are deionized water (21%), electricity production (9%) and heat from natural gas (7%).

Finally, main sources of water depletion in biomethanol are syngas production (52% equivalent to 1.7E+04 m^3), electricity production (11% or 3.6E+03 m^3) and deionized water production (7% equal to 2.4E+03 m^3). It is important to note that the inflow of wastewater that is being recycled in this process diminishes the environmental impact of biomethanol on water depletion.

4.3.5 Human toxicity – carcinogenics

As shown in Figure 4.7, the two DAC methanol options score significantly higher on human toxicity – carcinogenics than the other two alternatives. This is most likely linked to mineral extraction necessary for wind electricity production and is also reflected in the results. Electricity production accounts for 82% of NG option, comprised of 59% from CO_2 electrolysis, 21% from water electrolysis and 2% methanol synthesis. Similarly, electricity is responsible for 83% of human toxicity – carcinogenics of BM alternative, corresponding to 60% from CO_2 electrolysis, 21% from water electrolysis and 2% from methanol synthesis. Another contributing factor in these fuel alternatives was potassium hydroxide (11% for both alternatives 1a and 1b).

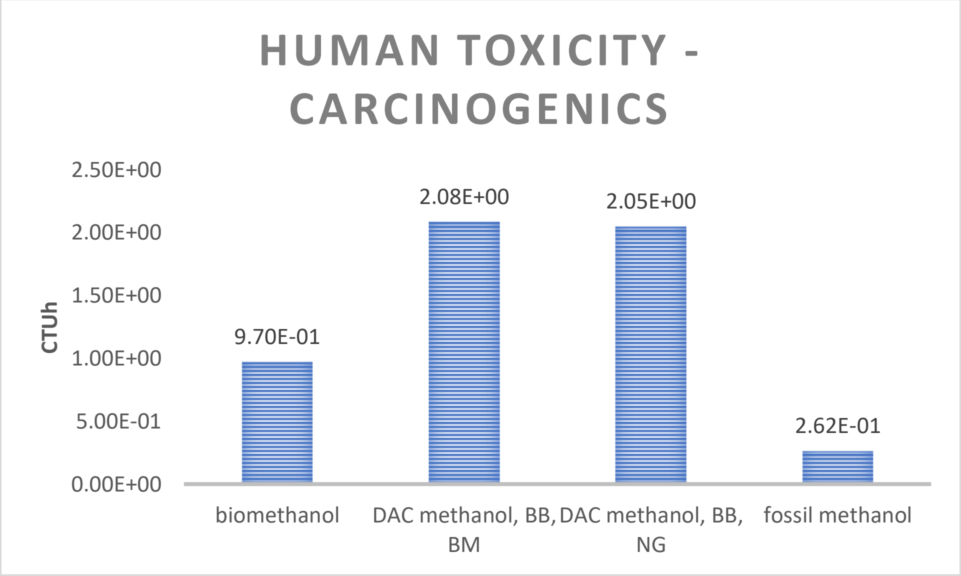


Figure 4.7: Characterization results for human toxicity - carcinogenics, for 4 alternatives, based on an annual production of 16.7 kt of methanol.

Biomethanol mainly contributes to this impact category with syngas production (69%), electricity production (20%) and molybdenum production (10%). Similarly, fossil methanol shows most impact from natural gas usage (38%), electricity production (20%) and molybdenum production (18%).

4.3.6 Human toxicity – non-carcinogenics

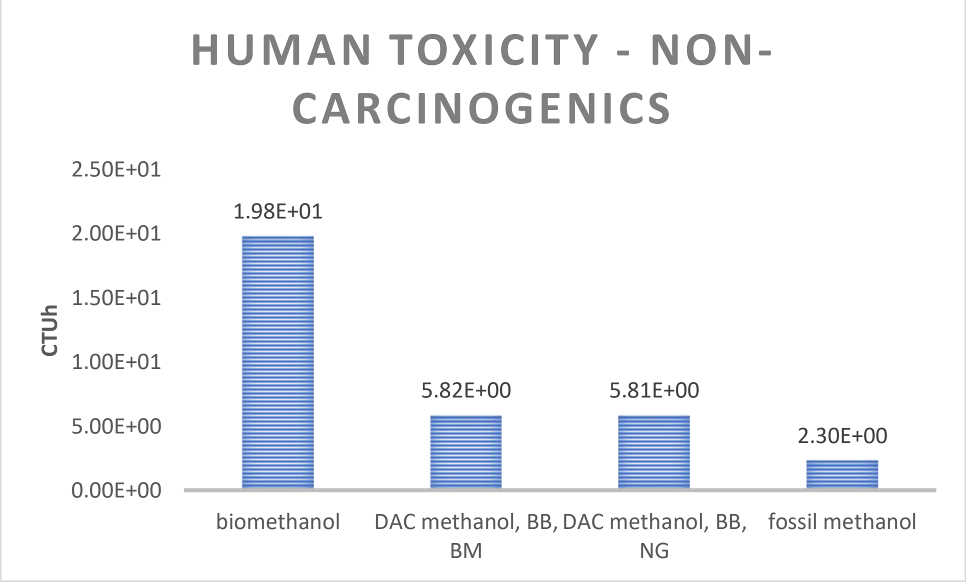


Figure 4.8: Characterization results for human toxicity - non-carcinogenics, for 4 alternatives, based on an annual production of 16.7 kt of methanol.

As can be observed from the vertical axes of Figure 4.7 and Figure 4.8, human toxicity levels in terms of non-carcinogenic substances are lower than emissions of carcinogenics, by an order of magnitude. Unlike carcinogenics, non-carcinogenic toxicity seems to originate from biomass. This can be seen by the prevalence of impact from biomethanol, although only reflected to a limited extent in DAC methanol BM.

In line with this, biomethanol registers the largest impact contribution in syngas production (17.3 CTUh, equal to 87%). The second most contributing process is molybdenum production (1.3 CTUh, 6%). Due to an absence of data on other category indicators, DAC methanol BM shows the most impact in electricity production (2.9 CTUh or 49% from CO_2 electrolysis and 1.0 CTUh equal to 17% from H_2O electrolysis). As mentioned above, it is assumed that a part of this electricity is used for torrefaction of biomass. To validate this claim, DAC methanol BM contributions are compared to DAC methanol NG.

The three main contributing factors in DAC methanol NG are identical to those of the BM alternative, namely electricity from CO_2 and H_2O electrolysis and production of potassium hydroxide. While the impacts from KOH production are the same for both alternatives, leading to 1.1 CTUh, and so are the burdens from water electrolysis (1.0 CTUh), there is a minor difference in human toxicity impacts from CO_2 electrolysis. Electricity used in this process in DAC methanol NG leads to 2.8 CTUh, while the same flow in BM alternative results in 2.9 CTUh. As the presence of biomass vs natural gas is the only flow distinguishing these alternatives, it is reasonable to assume that the source of impact deviation is, indeed, the torrefied biomass input.

Finally, human toxicity – non-carcinogenics from fossil methanol originates from molybdenum production (1.3 CTUh or 55%) and natural gas production (0.4 CTUh equal to 18%). This shows that both ecoinvent3.4 processes contain the same input of molybdenum for syngas processing.

4.3.7 Freshwater ecotoxicity

Figure 4.9 shows categorization results for freshwater ecotoxicity. It is obvious that DAC methanol BM leads to one and half times the impacts of its NG counterpart and 2.8 to almost seven times the ecotoxicity caused by other alternatives. A contribution analysis reveals that that 3.0E+08 CTUe, corresponding to 65% of the impact, comes from electricity deployed in CO_2 electrolysis. As this result is 1.9 times bigger than the electricity used for the same process in DAC methanol NG, it can be suggested that the difference originates from biomass torrefaction. Additionally, since biomethanol does not show as high ecotoxicity levels, it is assumed that the significant impact in DAC methanol BM indeed comes from the torrefaction itself rather than the input of biomass.

Other significant contributors to DAC methanol BM impacts on freshwater ecotoxicity are equal to those of its NG counterpart, namely electricity deployed in water electrolysis (5.7E+07 CTUe) and potassium hydroxide production for DAC (3.1E+07 CTUe). DAC methanol NG, however, only leads to 1.6E+08 CTUe from CO_2 electrolysis process.

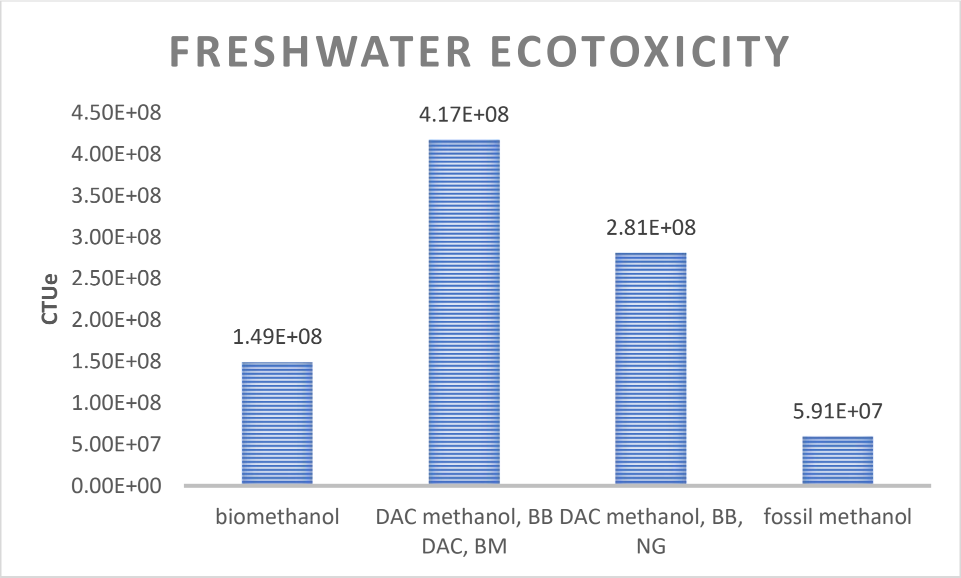


Figure 4.9: Characterization results for freshwater ecotoxicity, for 4 alternatives, based on an annual production of 16.7 kt of methanol.

When it comes to fossil methanol, the main contributing factor in its production is molybdenum (3.1E+07 CTUe or 53%), natural gas (1.2E+07 CTUe or 20%) and electricity (6.0E+06 CTUe equal to 10%). The last alternative examined, biomethanol, contributes to freshwater ecotoxicity with its syngas production (8.5E+07 CTUe or 57%), molybdenum production (3.1E+07 CTUe or 21%) and electricity production (1.9E+07 CTUe, equivalent to 13% of the impact).

4.3.8 Short summary of characterization results

The sections above examined the environmental performance of the four alternatives studied. The following section provides a brief overview of this environmental performance, summarized in a scorecard illustrated in Table 4.3.

Table 4.3: An overview of the environmental performance of four fuel alternatives examined. 1- the best, 4 - the worst. CC - climate change, LU - land use, RDM - resource depletion - mineral, fossils, and renewables, RDW - resource depletion - water, FWE – freshwater ecotoxicity

Alternative	CC	LU	RDM	RDW	HTC	HTNC	FWE
DAC methanol, NG	2	1	4	2	4	3	3
DAC methanol, BM	1	3	3	3	3	2	4
biomethanol	3	4	2	4	2	4	2
fossil methanol	4	2	1	1	1	1	1

As seen in Table 4.3, production of DAC methanol, NG does lead to a significant level of captured carbon dioxide, and thus, reduces the ambient CO_2 emissions before its use and concurrent combustion. This alternative also uses the least land, however, leads to worst resource depletion (mineral, fossils, renewables) impacts as well as human toxicity (carcinogenics). Nevertheless, an alteration of the DAC system by utilizing biomass instead of natural gas improves the environmental performance of DAC methanol on these two impact categories and leads to an additional capture of carbon dioxide. On the contrary, such a change in process design also affects the resource depletion (water) to a slightly larger extent, moderately worsens the land use and significantly aggravates the freshwater ecotoxicity.

It can also be noted that the fossil methanol production is a highly optimized process, leading to least environmental impact across the impact categories examined, with the exception for climate change. Finally, the production of biomethanol as a replacement of fossil methanol is only favourable when resource depletion (mineral, fossils, renewables), human toxicity (carcinogenics) and freshwater ecotoxicity are of concern. This fuel leads to fewer carbon dioxide emissions captured than CO_2-methanol, requires a significantly larger area of land and a larger water quantity to grow biomass and causes most human toxicity (non-carcinogenics) of the four alternatives investigated.

4.3.9 Sensitivity analysis of alternative 1a – DAC methanol BB, NG

As mentioned in the methodology, two scenarios were developed for the purposes of sensitivity analysis. These scenarios are the optimistic and the pessimistic scenario and consider all four sub-parts of the system, namely DAC, CO_2 electrolysis, H_2O electrolysis and methanol synthesis. The parameters applied and their respective values per scenario are shown in Table 4.4, below. While some of the parameters only examine different process efficiency – higher, same as currently reported, or lower, others, especially parameters reflecting catalyst quantities inspect a range of proposed amounts.

More specifically, NiAg catalyst deployed in CO_2 electrolysis was reported in varying ratios of Ni to Ag, ranging from 100:0 through 25:75, 50:50, 75:25 to 0:100 (Bettahar, Wojcieszak, & Monteverdi, 2009). For the baseline, 75% of nickel is mixed with 25% of silver. Additionally, potassium hydroxide electrolyte used in water electrolysis ranges between 1g/ 1kg H_2 and 2.5g/ 1kg H_2 (Delpierre, 2019). The baseline uses 1.5g per kilogram of hydrogen produced. Additionally, it was advised to use 0.01g of $Cu/ZnO/Al_2O_3$ catalyst per kg of methanol produced in the baseline. This is altered in the optimistic scenario, where lower requirements are assumed.

Finally, the cooling requirements of methanol synthesis are met by the input of water. While the baseline scenario assumes 95% recycling of the incoming flow of water, other quantities examined are 99% and 90% per optimistic and pessimistic scenario, respectively.

Table 4.4: Parameters per scenario chosen, distinguishing the main system parts (left column).
** input per system of Keith et al. (2018), corresponding to an annual production of 1.46 Mt CO$_2$. Note that production of the functional unit 16.7 kt of CH$_3$OH only requires 24.5 kt CO$_2$ input. The inventory data is scaled down by Open LCA to meet the reference flow.*

	Parameter	Unit	Scenario		
			Optimistic	Baseline	Pessimistic
DAC	captured CO2*	Mt/y	1.08	0.98	0.98
	solvent - KOH*	t/y	101309.4	112566	123822.6
	solvent - K2CO3*	t/y	27436.32	30484.8	3.35E+04
	heating req.*	m3/y	1.94E+08	2.16E+08	2.37E+08
	CaCO3 makeup*	t/y	26886.6	29874	32762.4
CO2 el.	NiAg ratio	Ni:Ag	100:0	75:25	50:50
	electricity req.	TJ/y	578.07	642.3	642.3
H2O el.	KOH electrolyte ratio	g/kg H2	1	1.5	2.5
	electricity req.	TJ/y	204.264	226.96	226.96
CH3OH syn.	Cu/ZnO/Al2O3 ratio	g/kg CH3OH	0.008	0.01	0.01
	water recycling rate	%	99	95	90

Based on these parameters, characterization results of DAC methanol BB, NG are examined per scenario. Figure 4.10 below provides an overview of all seven impact categories. As expected, the most favourable results are achieved in the optimistic scenario, while the most adverse impacts originate from the pessimistic scenario. We observe a rather low level of system robustness when examining the impacts on climate change, land use and resource depletion (mineral, fossils, and renewables) in the optimistic scenario. While the parameters are altered to a minor level, the changes that such alterations cause are equal to additional 56% in case of climate change, 25% in land use and 13% in resource depletion. Nevertheless, the remaining impact categories only experience a minor result variation, between 8% to 11%.

In the pessimistic scenario, the system shows a high level of robustness in all impact categories except for climate change. Here, 15% less carbon dioxide is captured. Nonetheless, the minor parameter alterations only lead to a 7% worse impact on the land use, 5% more impact on human toxicity (non-carcinogenics), 4% deterioration in terms of resource depletion (both impact categories) and 2% more environmental impact on human toxicity (carcinogenics) and freshwater ecotoxicity.

Additionally, as the contribution of processes in these results differs per impact category, further examination is provided, showing how selected processes impact each system subpart per scenario. Results of this contribution analysis are shown in figures 4.11 – 4.17.

Figure 4.10: Overview of characterization results of producing 16.7 kt/year of DAC methanol BB, NG per impact category, per scenario

Climate change

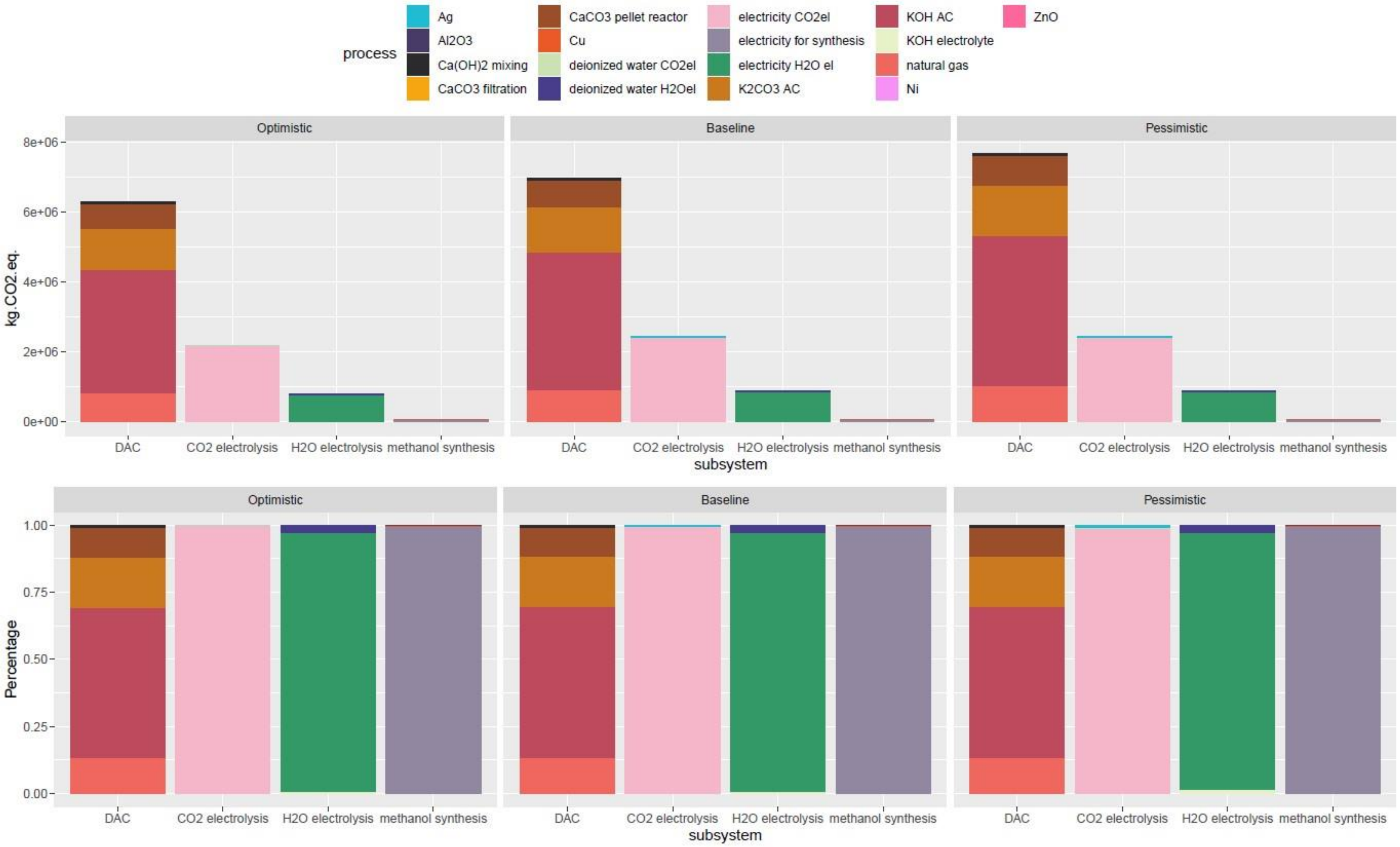


Figure 4.11: DAC methanol BB, NG – climate change impacts per scenario, per process subsystem

As shown in Figure 4.11, the most impact on climate change comes from DAC, between 67% and 69%. The major contributor to this result is the KOH solvent that serves as a means for capturing carbon dioxide. The rest of the DAC system is rather consistent in proportions, which is in line with 10% alterations in parameters chosen.

When it comes to the remainder of methanol production, an interesting observation that can be made is that as assumed, the quantity of silver in NiAg catalyst for CO_2 electrolysis leads to significantly higher impacts than its nickel counterpart. More specifically, a 75:25 ratio applied to the baseline results in 10% to 90% spread of kg CO_2eq. and a 50:50 ratio from the pessimistic scenario leads to 3% to 97% split from Ni and Ag, respectively.

Additionally, the share of kg CO_2eq. between CO_2 electrolysis, H_2O electrolysis and methanol synthesis is almost entirely made up of electricity contribution, which is why the proportion between these subsystems is in line with the electricity input in each.

Furthermore, it is important to note that all these impacts are compensated by the capture of carbon dioxide via DAC. Moreover, additional carbon capture is achieved by employing this type of methanol production, although the decarbonization potential of the DAC methanol depends directly on its utilization.

Freshwater ecotoxicity

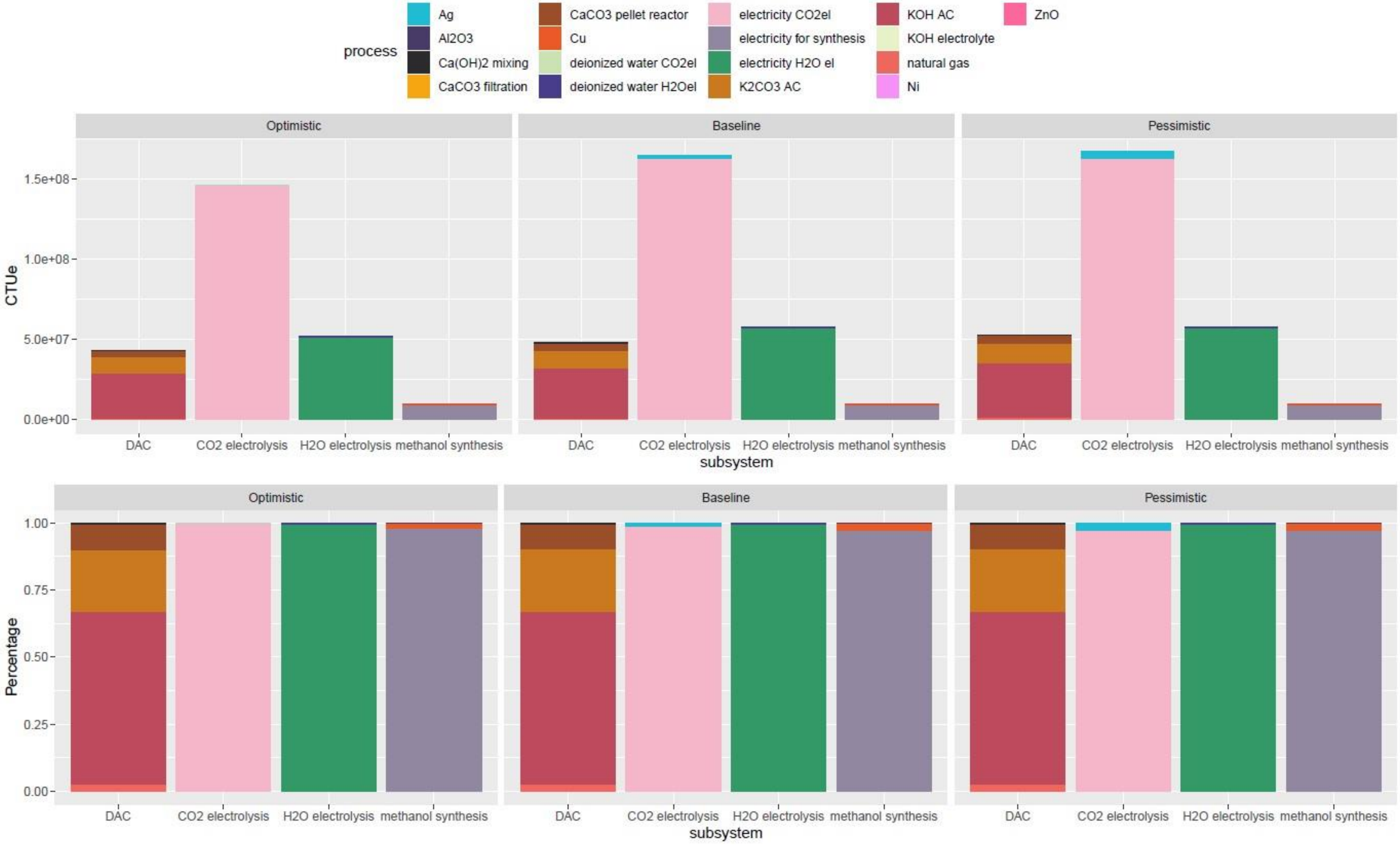


Figure 4.12: Freshwater ecotoxicity impacts of DAC methanol per scenario, per system subpart

Although we observe that the catalysts have a more significant impact on freshwater ecotoxicity than they do on climate change, the extent to which they influence the environmental performance of DAC methanol is very limited. Instead, the vast majority of freshwater ecotoxicity is caused by electricity production. In the optimistic scenario and the baseline, the electricity production is responsible for 82% of freshwater toxicity impacts, while in the pessimistic scenario, the electricity production adds up to 80% of freshwater toxicity. Proportionally, 58% comes from the CO_2 electrolysis (or 57% in case of pessimistic scenario), 20% from the water electrolysis and only 4% from the methanol synthesis (3% in the baseline). This is in line with the inputs of electricity required for each of the processes.

Interestingly, natural gas input influences the freshwater toxicity only to a limited extent. On the other hand, around 90% of impacts of DAC production come from potassium hydroxide and proportion of potassium carbonate that was missing in the material balances indicated by Keith et al. (2018).

Human toxicity – carcinogenics

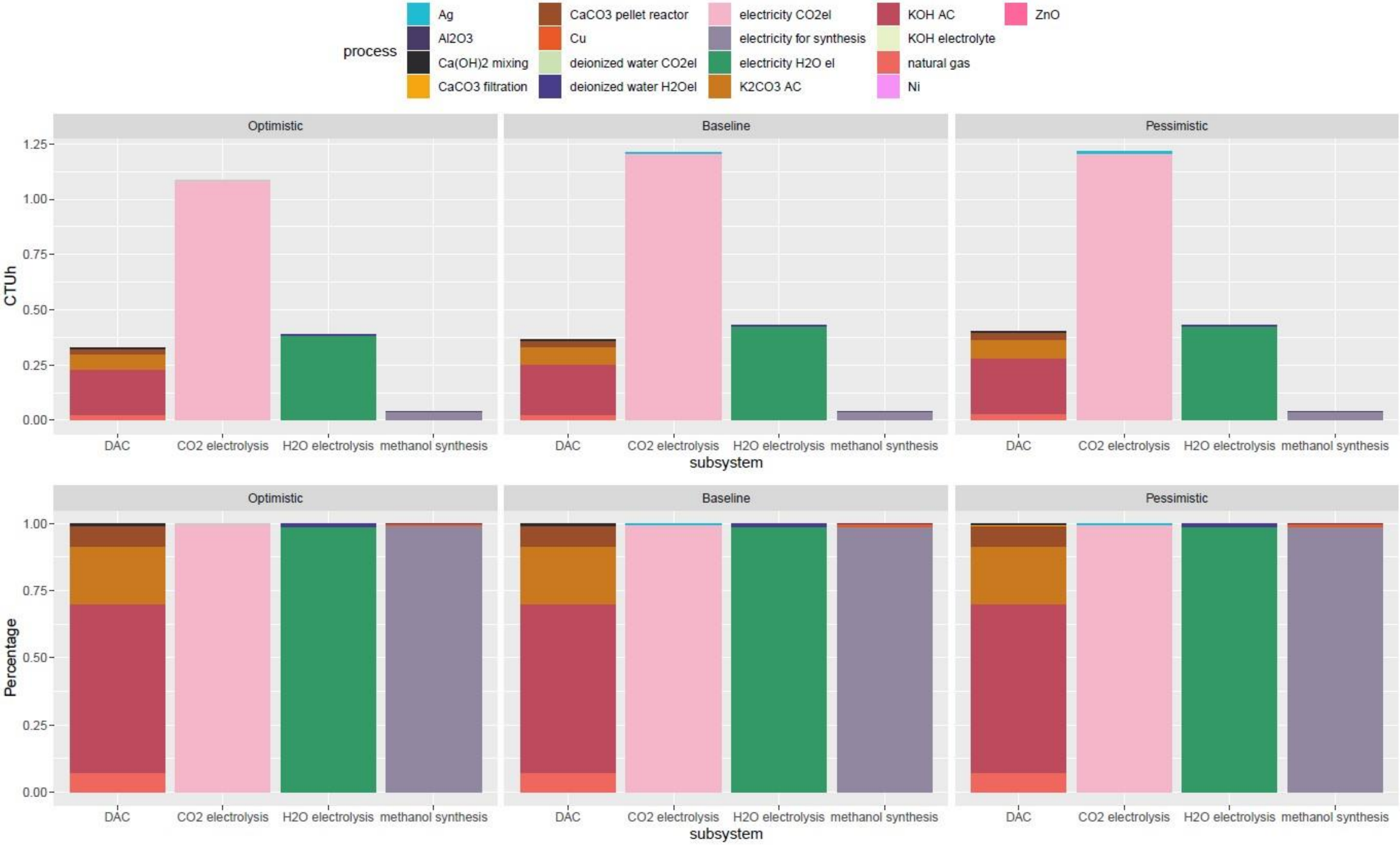


Figure 4.13: Human toxicity – carcinogenics impacts of DAC methanol per scenario, per system subpart

When it comes to the origin of human toxicity – carcinogenics in the production of DAC methanol, the main source can be found in the electricity production. This is consistent with freshwater ecotoxicity and human toxicity – non-carcinogenics, shown below. It can be assumed that the source of these environmental emissions comes from the production of metals and rare earth materials needed for the construction of wind turbines, which are the source of electricity in this model. As reported in the freshwater toxicity section, the second largest impact comes from the liquid solvent of KOH used to bind carbon dioxide from the air and a proportion of K_2CO_3 added to the system to balance the mass flows. Moreover, the extent to which catalysts impact the environmental performance of DAC methanol is even smaller when it comes to human toxicity – carcinogenics.

Human toxicity – non-carcinogenics

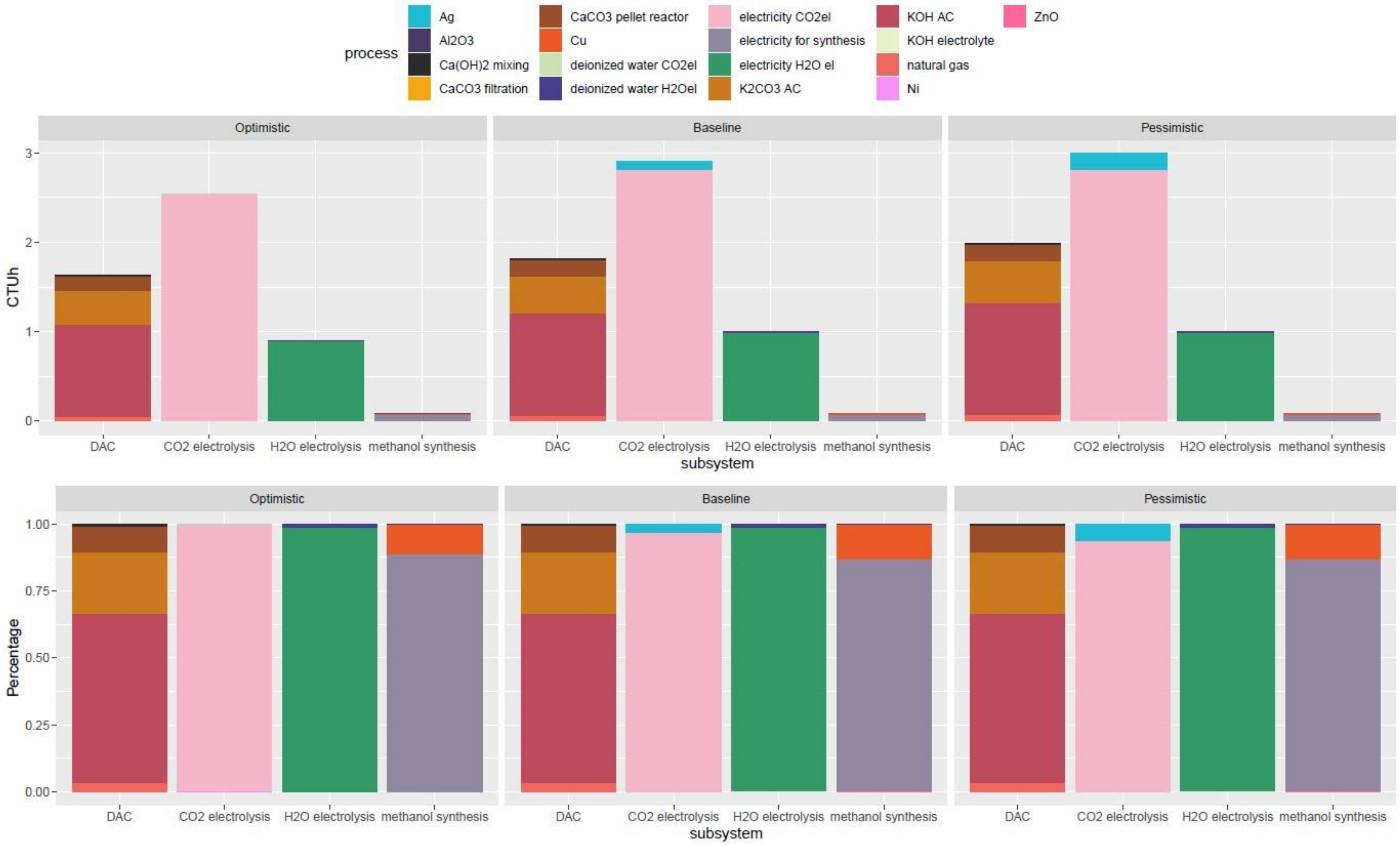


Figure 4.14: Human toxicity – non-carcinogenics impacts of DAC methanol per scenario, per system subpart

When inspecting human toxicity – non-carcinogenics, especially the vertical axis values, it can be observed that these impacts are significantly larger than those of carcinogenic character. The most impact here comes from electricity production. Nevertheless, we notice that air contacting, containing potassium hydroxide and potassium carbonate, has a more severe impact than that of electricity used in water electrolysis, combined with that of methanol synthesis.

Additionally, usage of silver as a part of the catalyst for CO_2 electrolysis process leads to more human toxicity than the entire methanol synthesis process. Considering the limited amount of catalyst applied in CO_2 electrolysis, namely 38.6 kg/year, and the energy requirements of the methanol synthesis process (17.7 TJ/year), production of which requires mining of metals and rare earth materials, it is interesting to observe rather significant impacts from silver usage on human toxicity – non-carcinogenics.

Land use

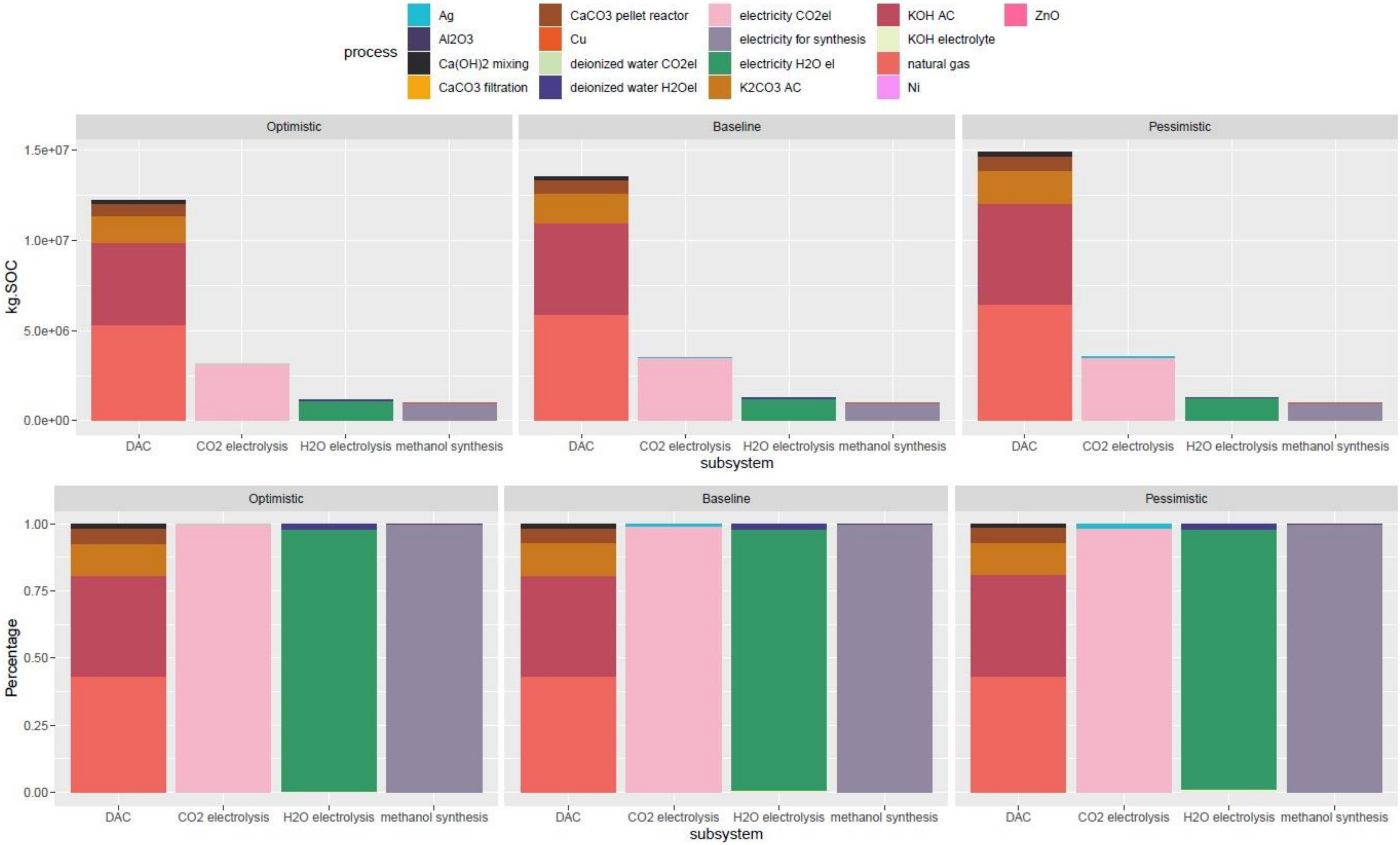


Figure 4.15: Land use impacts of DAC methanol per scenario, per system subpart

Unlike the previous category indicators, electricity scores relatively low on land use. It can be assumed that this result is linked to the off-shore nature of the wind power used in the system. Additionally, it is quite surprising that the potassium hydroxide usage for carbon dioxide binding leads to almost as much impact on the land use as natural gas combustion for calcination purposes. Again, catalysts almost do not impact the land use, with an exception of silver in the CO_2 electrolysis, although the extent of it is limited. Even though the total impact changes per scenario, proportions stay rather constant, with the exception of silver, as it is not used in the optimistic scenario.

Resource depletion – mineral, fossils, renewables

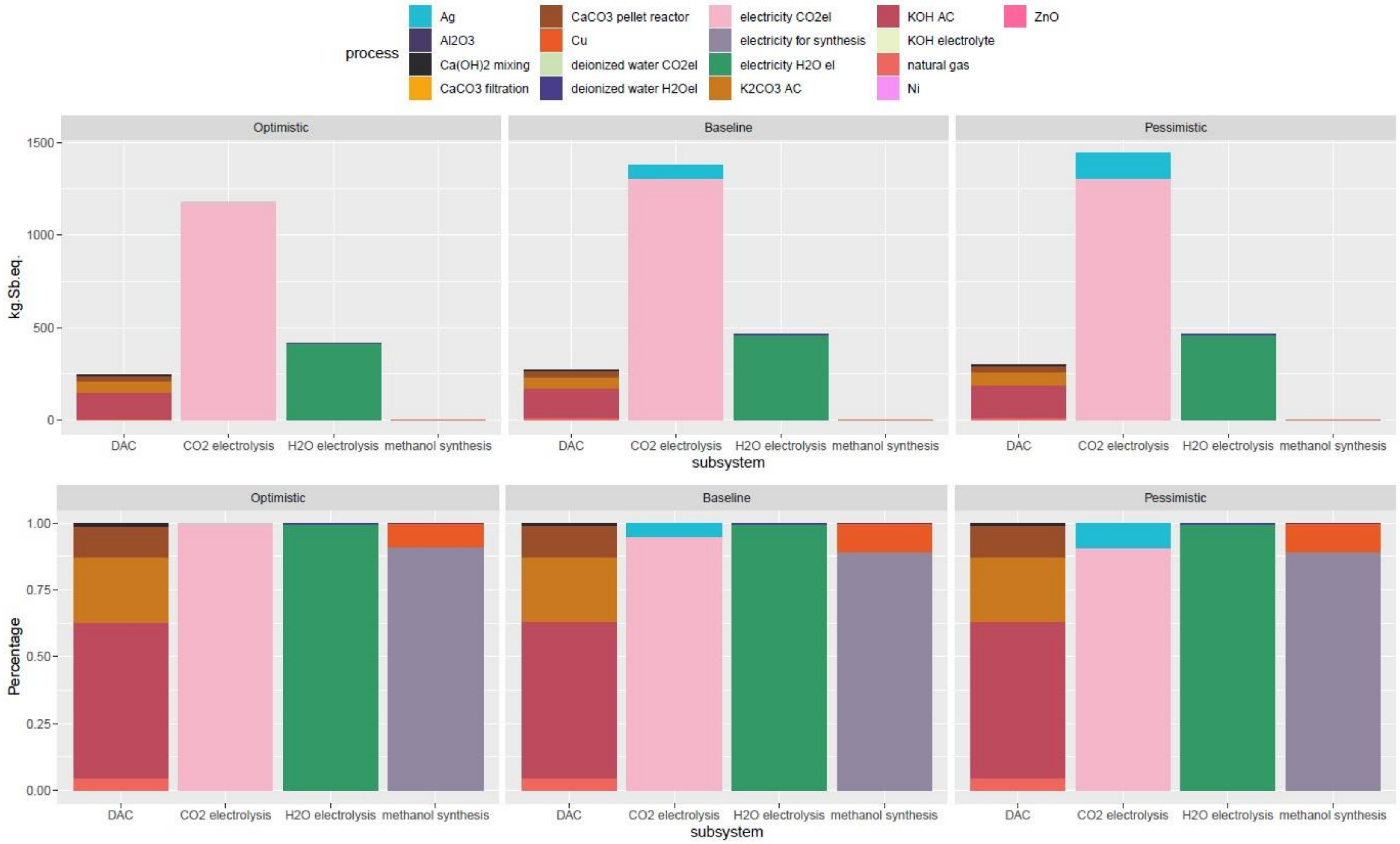


Figure 4.16: Resource depletion - mineral, fossils, renewables impacts of DAC methanol of DAC methanol per scenario, per subsystem

The main source of impact on resource depletion – mineral, fossils and renewables, comes from the electricity production from wind. This seems logical, as a broad range of materials is employed in its production. Nevertheless, while natural gas production for calcination seems of relatively low impact, if we compare the required stream of natural gas, i.e. 1.9TJ/year to, for instance 17.7 TJ/year of electricity for methanol synthesis from wind power, the impact per TJ/year is 24 times larger in case of natural gas than when using wind power.

Additionally, the catalyst application also leads to resource depletion. Unlike other impact categories, usage of $Cu/ZnO/Al_2O_3$ catalysts in methanol synthesis leads to proportionally more resource depletion than NiAg utilization in CO_2 electrolysis. Finally, potassium hydroxide solvent and potassium carbonate affect the environmental performance of the DAC system to a larger extent than that of natural gas, which seems quite interesting. It suggests that switching the solvent for carbon capture for a substance with lower environmental impacts can lower the resource depletion performance of the DAC to a larger extent than changing the source of heat.

Resource depletion – water

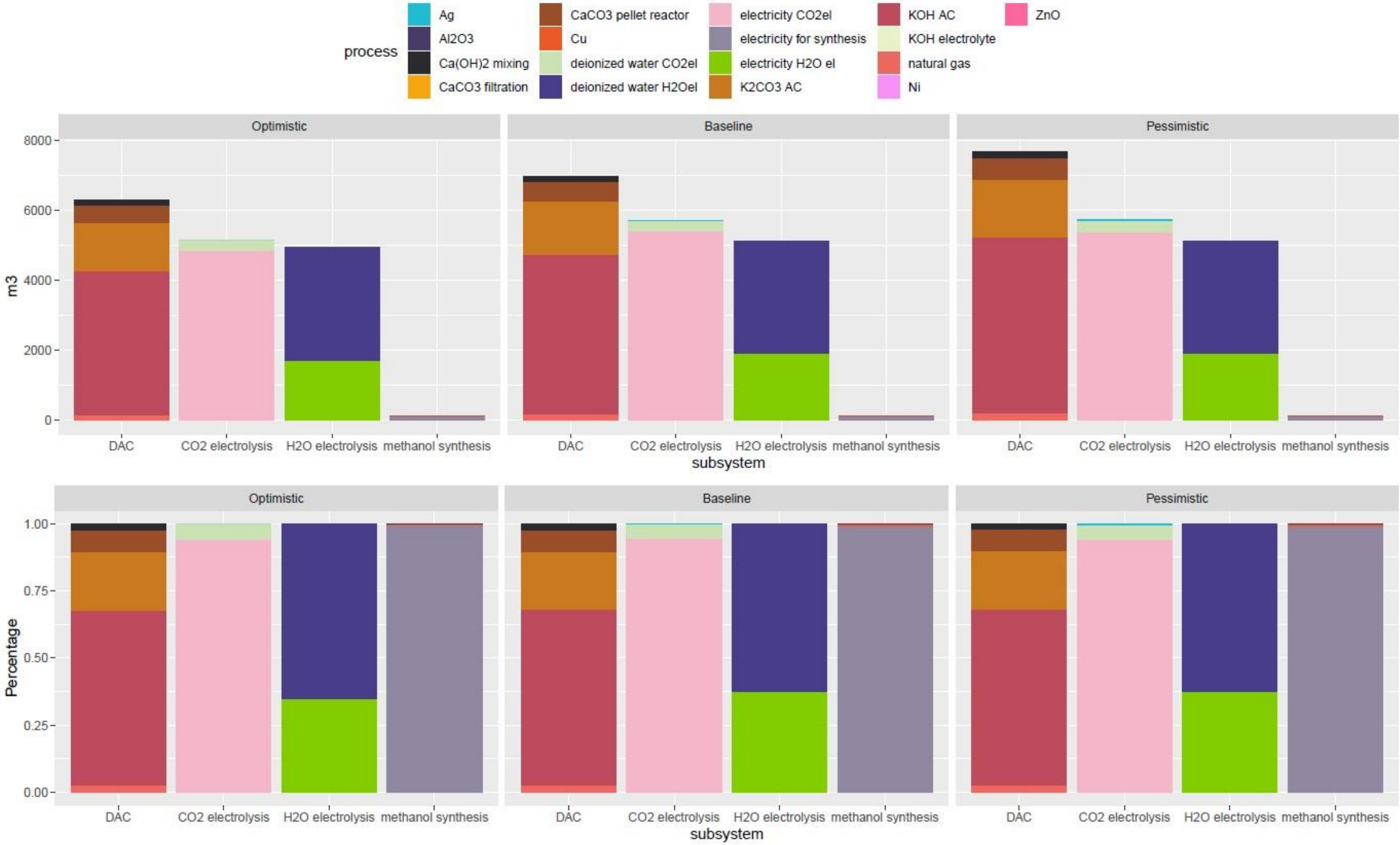


Figure 4.17: Resource depletion impacts of DAC methanol per scenario, per system subpart

Finally, as expected, a significant proportion of water depletion comes from the usage of deionized water in both electrolyses processes. What is surprising, however, is that wind electricity also requires rather high levels of water and so does the production of potassium hydroxide and potassium carbonate. As in most of the previous impact indicators, the proportions of contribution are quite constant, only the total impact varies.

The following chapter discusses these results in light of methodological steps and assumptions taken.

5. Discussion

This chapter provides a discussion of the implications of the methods applied, together with assumptions made, and their impact on the results of this research. Evaluation is given per research objective, even though some of the assumptions taken could have influenced multiple objectives. Additionally, the last section provides an overview of the scientific debate on carbon capture and utilization versus carbon capture and storage, as the production of DAC methanol falls under the umbrella of CCU.

5.1 Data analysis

5.1.1 Implications of the methodology chosen for data analysis

As mentioned in the methodology chapter, a two-level data analysis was undertaken. The level two opened the black box of DAC technology and enabled to cross-check recently published data by Keith et al. (2018) on the capture system operated by Carbon Engineering. Throughout the research, the author was introduced to a fellow researcher Alexander Caskie, who examined the DAC data of Keith et al. (2018) with the usage of the Aspen software. While comparing the data gained, it became clear that the way of computing these flows (i.e. manually or through the software) and the assumptions adopted for such calculations led to varying sizes of the mass flows. This sensitivity of data to assumptions could have influenced the total impact results and also process contributions within the DAC. Nevertheless, unless a revised article with correct figures is published by Keith et al., determining how the operation of Carbon Engineering's DAC really looks is not feasible. The author attempted acquiring more accurate data directly from David Keith; however, was told that Carbon Engineering is currently not considering sharing any more information.

In order to balance the inaccurate mass flows within the DAC systems and to examine the chemical reactions where no literature on actual yields was available, high process efficiency was assumed and calculated based on number of mols available. A basis for this was a hypothesis that on an industrial scale, the performance of processes is highly optimized. Should that not be the case, then some of the processes that were not balanced originally might require an even larger inflow of virgin material, causing more significant overall environmental impacts.

While the two-level perspective on DAC allowed to correct the errors in reported flows and led to the compilation of comprehensive inventory data, the final model works with a black-box approach with adapted flows, as the full model did not yield correct inventory results even after its thorough examination and implementation of hypotheses.

The rest of the CO_2-methanol system was only analysed on level one, relying on data reported by Torri (2019). It was assumed that the system represents the state of the art of this type of methanol synthesis. Should this not be the case, other discrepancies are possible.

5.1.2. Results of data analysis

Since the fines filter was modelled as a closed-loop recycling process, where no water input is needed, a dilemma on which mass to model (namely, 389,000 reported, 7,000 selected by a fellow researcher, or any other quantity), was avoided. Nevertheless, it is likely that some initial water input is required, leading to somewhat underestimated results, especially those of resource depletion – water.

Moreover, an additional flow of calcium hydroxide, part of which does not react, can lead to additional costs of circa 2900 USD/hr based on prices indicated at Alibaba.com. Furthermore, if this flow gets recycled within the system, it would mean that the environmental impacts of DAC in this thesis are slightly overestimated. Nevertheless, calcium hydroxide is not a significant source of environmental impact in this product system, as can be seen in the sensitivity analysis and contribution graphs presented in chapter 4.

The economic concern, although not a focal point of this thesis, also applies to unreacted calcium oxide leaving the slaker. However, as no virgin calcium oxide is imported from the system, it is assumed that the environmental performance is not affected by it. The same concern is relevant to recirculated potassium carbonate from the slaker to the calciner. However, these two substances were fully recycled in our model and did not require primary material from the background. Therefore, the issue of the impact of recycling on the environmental performance is negligible for our model.

Furthermore, as discussed in the results, the DAC system described by Keith et al. (2018) uses natural gas feedstock for additional carbon dioxide production. The proportion of CO_2 captured from within the system is staggering, equal to one-third of all carbon dioxide compressed. This finding makes the implementation of Carbon Engineering's system questionable, as it produces CO_2 to capture ambient CO_2 and thus promotes continued use of fossil fuels. It is essential to investigate whether suggested replacement by biomass is suitable, or why capture of 0.98 Mt/ year instead of 1.46 Mt/ year with usage of renewable energy is not a currently applied practice.

5.2 Life cycle assessment of DAC methanol

5.2.1 Goal, scope, function

The scope of this thesis in terms of geographic location was the Netherlands. Throughout the research, it was assumed that the entire process of methanol production takes place within one location around the area of Port of Rotterdam, diminishing the need for transport, which would otherwise increase the impacts of the reference flow. Nevertheless, as such a production plant is currently a hypothetical one, it did not seem of significant relevance to pick a specific location per each subsystem. This is also closely linked to the cut-off of machinery needed. Had the transportation been considered, necessary infrastructure would also need to be modelled for the sake of consistency.

Additionally, as stated in the methodology section, this study considered the production up until the well point. However, the well, in this case, is the endpoint of the DAC methanol production line rather than the market for fuel; reflecting the transportation considerations.

Additionally, for the modelling on CO_2-methanol, it was assumed that the distillation requirements are already included in the catalytic synthesis process, as this step of production was not distinguished in the data reported by Torri (2019), yet her process counts with distillation.

Regarding the functional unit studied, the model built produces 16.7 kt of CO_2-methanol per year. The selection of this quantity originates from process data availability. More specifically, rather high-quality data from Torri (2019) provides information on the production of 16.7 kt of methanol. From the perspective of global fuel demand, this is a negligible quantity. Nevertheless, as it was assumed that the process of methanol production is not linear, this quantity was examined to preserve the process data accuracy. Acquiring process data on large CO_2-methanol production and linking it with available carbon dioxide supply of 1.46 Mt/ year from the DAC is recommended for future research.

The alternatives 2 and 3 were fully adopted from ecoinvent3.4. This means that no major data analysis of these alternatives was undertaken as one could claim that such a rich database is of sufficient data quality and resolution. Nonetheless, when comparing the data description of these two alternatives available on ecoinvent's website, it was observed that the data of methanol from biomass is of lower resolution than that of methanol from methane steam reforming. Using industrial data for these production practices could diminish some of the uncertainties. For instance, a somewhat surprising finding was the presence of deionized water in both processes. This feedstock is also present in the production of DAC methanol. However, that is caused by high-purity water requirements for electrolyses.

When it comes to alternative 1b, the feedstock of biomass chosen contains very limited data on emissions and impacts resulting from its usage. Therefore, it is unclear how realistic the environmental impacts related to biomass production were. Furthermore, it was deducted that this stream of biomass is an output of the torrefaction process, as its indicated lower heating value (14.7 MJ/kg) was rather high for a flow, which usually contains a high percentage of moisture, causing its LHV to drop.

It would be interesting to compare this feedstock with other sources of biomass, even though this flow was the only biomass product available in the database. The reason for such comparison would be to determine an optimal point between LHV and quantity of biomass required, from the environmental perspective. It can be assumed that a source with higher moisture content would require a more abundant biomass inflow, leading to a more significant impact on land use and resource depletion (water). Nonetheless, a possibly lower impact on resource depletion (mineral, fossils and renewables), could be achieved as less energy would be applied to its pre-processing by employing torrefaction. The extent to such impact alterations is, however, unknown to the author.

5.2.2 System boundaries and multi-functionality

As mentioned in the methodology, some of the emissions occurring in the foreground processes, such as emissions of carbon dioxide from CO_2 electrolysis, were not modelled, as it was only later discovered that this system does not process all of the CO_2 fed in. Incorporation of this emission data would lead to slightly diminished climate change results of DAC methanol. However, as the level of emissions in comparison with the level of carbon dioxide used in the process is expected to be relatively low, it is assumed that the product system would still record negative values on this impact category.

Additionally, oxygen produced by electrolyses could be considered an environmental emission. Nevertheless, as this flow has an economic value, it was assumed that it is being sold, even though machinery necessary for such sale was not modelled.

In line with this, machinery is cut-off in the overall CO_2-methanol system due to a lack of data, however, it creates somewhat of an inconsistency with other alternatives, which contain 'methanol factory' input. For future studies, implementation of this type of data would lead to a more precise assessment of the total impact.

5.2.3 Data collection

The power requirements of the CO_2-methanol system reflect a continuous wind power supply, assuming the presence of a network, which levels out the intermittency of wind power, inherent to this renewable energy source. Had intermittency been implemented in the model, it would more closely reflect reality and very likely also increase the environmental impacts of the DAC methanol production.

It is important to note that the source of wind power significantly affects the environmental results of DAC methanol. An error in modelling of DAC methanol, BB, BM with power from 3> MW onshore wind turbines has led to toxicity levels 12 times higher than those of the NG alternative with power supplied by 1-3 MW offshore wind turbines, both sources located in the Netherlands. This mistake was corrected, after which the results of the two alternatives were almost identical, and the presented results reflect power supplied by 1-3 MW offshore wind turbines.

Due to a lack of data on the amounts of NiAg catalyst and $Cu/ZnO/Al_2O_3$ catalyst, a rough estimate was made based on a conversation with a process engineer. Consequently, 0.01g of catalyst per kg of product is used for CO_2 electrolysis and methanol synthesis. This is two orders of magnitude lower than the quantity of electrolyte reported by Delpierre (2019) and applied in H_2O electrolysis process. In case of better data availability on applied catalyst quantities, it is recommendable to substitute the values in the model by measured amounts.

When it comes to water for methanol synthesis cooling, it is possible that a lower temperature feedstock is used rather than the 20 °C modelled, which would lead to a smaller quantity of water required. Also, the selection of seawater reflects the location of the production plant in the industrial area of Port of Rotterdam. Using freshwater from river basis was also considered, as another important industrial area in the Netherlands is located in Geleen, Limburg. This would imply utilizing water from river Maas and it would potentially indirectly suggest higher ambient CO_2 concentrations, possibly leading to post-combustion capture from flue gas. Nevertheless, the focus of this thesis is DAC and as the CO_2 electrolysis technology is being developed at the Delft University of Technology, close to Rotterdam, the assumption on locating the plant in the Port of Rotterdam and, therefore, using seawater, was applied. It is possible that using freshwater sources would increase the overall freshwater ecotoxicity results of DAC methanol and possibly also other indicators.

5.2.4 Modelling choices

Alternative 1b – DAC methanol with biomass instead of natural gas assumes that such replacement is feasible. However, precise reasons for using natural gas in the DAC system are unknown and only speculations can be made. Therefore, there is a possibility that Carbon Engineering's DAC cannot be run on energy from biomass combustion. Still, exploring such an alteration showed a potential of DAC technology when decoupled from fossil fuels.

In line with the linearity of LCA, modelling explained in the methodology, preheat 1 and preheat 2 were split and additional 'dummy' processes were created. However, this was not the case for the pellet reactor. Although the pellet reactor case is somewhat different, as unlike the preheats it has one primary function, the fact that the incoming flows are also concurrently being separated and filtered suggests that exploring if there is any consequence of this 'unsplit' process could be examined.

5.2.5 Scenario building

Looking at the electricity requirement parameter of scenarios created, it was assumed that data reported by Torri (2019) reflected the current manufacturing practices. Instead, it was later discovered that these numbers were a result of process optimization, therefore, rather optimistic. Because of that, it is possible that within the pessimistic scenario, electricity needed would be greater, contrary to the basis of the narrative behind this scenario. Consequently, the results of the pessimistic scenario might be underestimated.

Additionally, the extent of parameter alteration is in the majority of cases selected randomly and does not reflect the current market trends. While altering the parameter values to represent the future expectation better would lead to more accurate predictions, the scenarios still serve its primary purpose, namely, to reflect the system's sensitivity to changes.

As most parameter changes were minor, it is quite surprising to observe that they lead to major differences in the impact results of climate change, land use and resource depletion (mineral, fossils, and renewables) within the optimistic scenario. Additionally, a major difference in result can also be noted in the climate change result of the pessimistic scenario. This could point to the system's low level of robustness. Nevertheless, such deviations are not observed in the remaining impact categories of the optimistic scenario, nor the pessimistic scenario. Instead, the result variations are consistent with the low level of alterations. Therefore, based solely on this sensitivity analysis, it cannot be argued against the robustness of the product system.

5.2.6 Inventory assessment

As mentioned in the results section, two discrepancies were identified in the contribution analysis of the ecoinvent alternatives. Namely, the climate change results of biomethanol are off, as the negative impacts are larger than the positive, however, the system does not sum them up correctly. A suggestion was made that this might be caused by the way of building the product system. Namely, the author created an empty process, where 16.7 kt of 'methanol, from biomass' was fed and without adding any other flows or applying any sort of allocation, a flow out called 'biomethanol' with the value of 16.7 kt was produced. As these processes were identical, it does not appear that this would be the source of the problem. Nevertheless, another product system was created, directly from the ecoinvent 'methanol, from biomass' and also from 'market for methanol from synthetic gas', input of which is also biomass. As shown in figures C.1 and C.2 in Appendix C, the results do not add up and neither do their contributions.

Even though the numbers for climate change impacts do not add up, that is not the case for the rest of the impact category results for biomethanol. No issues were identified in the remaining six impact categories examined.

Nonetheless, when it comes to methanol from methane steam reforming, also directly adopted from ecoinvent3.4, similar issues were found in the resource depletion – water. Once again, a new product system was created, directly from the ecoinvent process and compared with another alternative, without success or indication of the nature of the problem. This is shown in figures C.3 and C.4 in Appendix C.

Just like in the case of biomethanol, the remaining characterization results are in order, their contributions add up and so do the values of each process responsible for a proportion of the impact.

As different ways of creating a product system did not resolve the issue, a hypothesis was made that a possible source of the problem can be ecoinvent's data for these two processes and their impacts, a potential damage to the zolca file used to import the ecoinvent database, or a problem with the OpenLCA software (version 1.8.0) itself.

An additional investigation was undertaken, in OpenLCA version 1.10.1. Nonetheless, using a newer version of the program yielded the same results as reported above. Various trials were undertaken, with allocation 'As defined in processes' and also with no allocation, not leading to any change in the results.

Moreover, ecoinvent reports on these fuel alternatives were examined, as they show some of the process contributions. However, the contributions reported were far off the contributions originating from the model.

Finally, an alternative impact assessment method, more specifically ReCiPe Midpoint (H) version 1.11, was applied. When inspecting the contribution results of biomethanol on climate change, it was observed that the percentage contributions do total 100% (see figure C.5). This was also the case for fossil methanol and its impact on water depletion (figure C.6). Because of that, the impact factors in this assessment method were examined and compared with those of ILCD midpoint 2011, version 1.0.10, applied throughout this thesis.

An important observation was made that while ILCD recognizes six types of biogenic carbon with a negative impact on climate change, no negative carbon dioxide contribution is contained in ReCiPe. Additionally, ILCD's resource depletion – water also contained negative impact factors, while ReCiPe did not. Furthermore, as climate change contributions reported by ecoinvent are based on IPCC impact assessment method, this method was also analysed. Here, the only negative carbon dioxide emission was CO_2 to soil. This is why only positive impacts on climate change are reported by the ecoinvent.

As shown in Appendix C, the total impact of biomethanol on climate change based on ReCiPe is equal to 1.11E+7 kg CO_2eq., which is only a 12% deviation of the positive results recorded by ILCD. Similarly, the difference between the results from ILCD assessment of water depletion and those of ReCiPe is circa 10%. This suggests that both assessment methods lead to an almost equal positive impact result. Nevertheless, ILCD also calculates the negative impacts, shown in climate change results of biomethanol. In addition, it is likely that the source of lower water depletion in ILCD assessment also comes from negative emissions, although not displayed in the contribution results.

Therefore, it is assumed that when calculating the process contributions of ecoinvent processes, OpenLCA does not sum the negative emissions correctly, which leads to incorrect relative contributions. Consequently, the processes displayed in the contribution analysis do not add up to 100%. For the purposes of this thesis, it is assumed that biomethanol production leads to -2.4E+07 kg CO_2eq impact on climate change and that fossil methanol production causes water depletion of 1.11E+4 m^3, both reported in chapter 5.2.

While in case of biomethanol and its impact on climate change the total impact also did not add up, this was not observed in DAC methanol, which also contained negative carbon emissions. It is assumed that this divergence comes from varying carbon dioxide input. More specifically, ecoinvent's biomethanol contains biogenic carbon, yet DAC methanol utilises carbon dioxide resource from air.

The issue of incomplete impact assessment methods, specifically of missing biogenic carbon, is also discussed by Mendoza Beltran et al., (2018). For their study, these authors extended their impact assessment method for biogenic carbon data from IPCC's Fifth Assessment Report (Mendoza Beltran et al., 2018). For future research, it is recommended to use an alternative impact assessment method complemented by negative impact factors. Results of such study should be compared with the results originating from ILCD. Moreover, modelling the system in an alternative LCA software is recommended to analyse whether correct contributions and total impacts are being displayed.

5.3 Evaluation of LCA's suitability

As explained in the methodology and further in the results section, having modelled the system using composite flows in combination with closed-loop recycling caused the software to calculate the inventory of the DAC system incorrectly. The author attempted to model the DAC in CMLCA software instead, but due to unidentified issues, the inventory results were highly overestimated. Therefore, the final results presented are based on black-box approach modelled in OpenLCA. At the same time, this black-box system is more accurate than it would be if the two-level analysis was not applied. For future studies, a combination of trials with CMLCA for the purposes of closed-loop recycling modelling and EASETECH, developed by Clavreul et al. (2014), for composite flows is recommended. Additionally, the theory on ‘mirroring effect’ presented in the results should be explored further.

The complications encountered in modelling of this product system are not to be interpreted as unfitness of LCA for evaluation of CO_2-methanol’s environmental performance. Instead, it is a reflection of the imperfect software available, which is not sufficient to model realistic industrial processes.

5.4 Scientific debate on carbon capture and usage vs carbon capture and storage

As explained in the sections above, CO_2-methanol examined in this thesis comes from the feedstock of carbon dioxide from the ambient air. This way of reusing the CO_2 is also known as Carbon Capture and Utilization (CCU). Although the premise of carbon dioxide recycling can be perceived favourably, some of the utilization options, such as fuels, only capture the CO_2 for a very limited time before getting released to the atmosphere again. That is why some scientists question the decarbonization potential of CCU. The paragraphs below compare CCU with Carbon Capture and Storage (CCS) and summarize the available information on the two types of technologies.

In order for CCS and CCU to be considered negative emissions technologies (NETs), feedstocks of required carbon dioxide need to come from biomass or DAC. Additionally, in the case of CCU, it is crucial to assure permanent carbon removal. According to Abanades, Rubin, Mazzotti and Herzog (2017), CCU removes fewer emissions than CCS, at a higher cost both in terms of technology, as well as climate change mitigation. Such a conclusion comes from the hypothesis that for CCU to be environmentally positive, it requires renewable energy sources, which could instead be deployed to substitute highly polluting power plants.

As in this thesis, Abanades et al. (2017) analyse a CO_2-to-methanol case study and argue that if carbon dioxide emissions are to be used for transportation, the maximum reduction achievable is equal to 50%. The reason for such a limitation is fuel combustion leading to recurring CO_2 emissions. Nevertheless, Abanades et al. (2017) also claim that if the source of CO_2 is DAC or natural photosynthesis, a closed carbon recycling loop can be achieved in CCU. They advocate for CO_2 storage or CCU as a short-term fossil fuel alternative as a means of transition, until more sustainable solutions are implemented on a large scale.

These findings are in line with Mac Dowell, Fennell, Shah and Maitland (2017), who report that CCU will have an insignificant impact on climate change mitigation, with the exception of enhanced oil recovery (EOR) technology. They find that focusing on CCU as an economic extension of CCS can substantially curtail CCS adoption, threatening the chances of meeting the set emission targets. According to their study, “CCU may prove to be a costly distraction, financially and politically, from the real task of mitigation”(Mac Dowell et al., 2017, pg. 243).

Kätelhön, Meys, Deutz, Suh, and Bardow (2018) suggest that CO_2 fuels store the same amount of carbon for the same period as their fossil counterparts. They recognize the potential of CO_2 fuels to increase energy security and lower import dependency of economies without fossil fuels abundancy. Nevertheless, the major opportunity for CCU they see is in carbon feedstock of the chemical industry, allowing for the production of large-volume chemicals, therefore, not as a transport input.

Nevertheless, an optimistic view on CO_2 fuels is given in a commentary by Kraan, Kramer, Haigh, & Laurens (2019), who propose the usage of solar fuels as it offers a circular way to reuse carbon dioxide, thus providing a boundless supply of fuel. According to these authors, the advantage of CCU over CCS lies in avoiding the need for 'active, government-lead coordination', and issues such as the need for new infrastructure and planning (Kraan et al., 2019). Nonetheless, to prevent global carbon dioxide emissions from rising, closing the carbon loop is a crucial part of their solution.

These concerns should be considered before opting for large-scale DAC methanol production for the purposes of alternative, more environmentally friendly fuel production.

Finally, an additional topic for future research recommended by the author is energy returned on energy invested (EROI). This would allow to assess whether the energy contained in DAC methanol compensates for the energy input required for its production.

6. Conclusions

This thesis examined the production of an alternative liquid hydrocarbon fuel, namely CO_2-methanol, produced by means of DAC, CO_2 electrolysis, H_2O electrolysis and thermo-catalytic synthesis. The reason for such research lies in a persistent growth in global energy demand, a significant share of which comes from liquid fuels, in the present context of global climate change.

In order to answer the main research question 'What is the comparative environmental performance of DAC methanol, natural gas methanol and biomethanol?' three research objectives were met. First, a two-level data analysis of DAC process engineering data published by Keith et al. (2018) was undertaken, revealing errors in mass flows within the system. This required additional inflows of virgin material to be calculated. Moreover, level 1 analysis of the remaining parts of CO_2-methanol production showed a lack of data on catalysts used and cooling water requirements. Therefore, an investigation into catalyst composition and quantity was performed, leading to the formulation of assumptions on this data. This was also the case for cooling water in the process of catalytic synthesis. Finalizing the data analysis led to a compilation of inventory data needed for an LCA model.

Second, a life cycle assessment was carried out based on data acquired. It was assumed that a yearly production of 16.7kt of four methanol alternatives took place. These fuel alternatives were examined on their impacts on climate change, freshwater ecotoxicity, human toxicity – carcinogenics and non-carcinogenics, as well as land use, resource depletion – mineral, fossils, renewables, and resource depletion – water.

The assessment showed that CO_2-methanol production up until the well point leads to negative CO_2 emissions. The extent of this positive climate change impact was almost two times larger than that of biomethanol. In contrast to these two fuels, fossil methanol production exacerbates climate change.

Inspection of freshwater ecotoxicity results suggests that CO_2-methanol production causes ecotoxicity levels almost five times as large as those of fossil methanol and almost twice as high as impacts of biomethanol production. Investigation of human toxicity – carcinogenics impacts shows significantly more severe effects on human health caused by CO_2-methanol production than by the production of fossil methanol (8 times more) or biomethanol (2 times more). Human toxicity – non-carcinogenics results are considerably better. Here, the CO_2-methanol production shows 2.5 times more impact compared to fossil methanol and only one-third of impacts related to biomethanol production.

Furthermore, evaluation of results on land use demonstrated a far better environmental performance of CO_2-methanol production compared to biomethanol (almost 16 times lower impact) and slightly better performance in comparison with fossil methanol (0.25 times lower impact).

Nevertheless, production of CO_2-methanol is responsible for 2.3 times more resource depletion – mineral, fossils, and renewables than biomethanol and almost 6 times the depletion caused by fossil methanol. However, the results also suggest that a DAC process alteration towards biomass combustion instead of natural gas combustion can diminish these impacts by a third. Considering the water depletion, CO_2-methanol affects this impact category to a larger extent than its fossil counterpart (by circa 60%), but less than the depletion caused by biomethanol production (56% thereof).

These results are to be interpreted with caution as a sensitivity analysis revealed that the product system responds to rather minor changes by a large difference in results in some of the impact categories examined.

The third research objective evaluated the suitability of LCA for the assessment of a product system as complex as this CO_2-methanol model. It can be concluded that while it is of societal relevance to analyse the environmental performance of industrial processes, and to do so in a manner that reflects the current manufacturing practices, the available LCA software cannot yet account for all intricacies, such as composite flow modelling and closed-loop recycling.

Finally, when deciding whether to produce CO_2-methanol fuel for climate change mitigation purposes, it is crucial to consider the short carbon capture time within such fuel. Unless a continuous large-scale carbon dioxide recirculation is assured, combustion of CO_2-methanol releases a significant share of the emissions captured.

7. References

Abanades, J. C., Rubin, E. S., Mazzotti, M., & Herzog, H. J. (2017). On the climate change mitigation potential of CO 2 conversion to fuels. *Energy Environ. Sci*, *10*, 2491. https://doi.org/10.1039/c7ee02819a

Atsonios, K., Kougioumtzis, M. –A., Grammelis, P., & Kakaras E. (2017). Process Integration of a Polygeneration Plant with Biomass/Coal Copyrolysis. *Energy&Fuels*, *31*, 14408–14422. Retrieved from https://pubs.acs.org/doi/pdf/10.1021/acs.energyfuels.7b02587

Bettahar, M. M., Wojcieszak, R., & Monteverdi, S. (2009). NiAg catalysts prepared by reduction of Ni2+ ions in aqueous hydrazine. II. Support effect. *Journal of Colloid and Interface Science*, *332*(2), 416–424. https://doi.org/10.1016/j.jcis.2008.12.068

BP p.l.c. (2018). *BP Energy Outlook - 2018 edition*. Retrieved from https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/energy-outlook/bp-energy-outlook-2018.pdf

Clavreul, J., Baumeister, H., Christensen, T. H., & Damgaard, A. (2014). An environmental assessment system for environmental technologies. *Environmental Modelling and Software*, *60*, 18–30. https://doi.org/10.1016/j.envsoft.2014.06.007

Daggett, D., Hadaller, O., Hendricks, R., & Walther, R. (2006). Alternative Fuels and Their Potential Impact on Aviation. *ICAS*. Retrieved from https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20060051881.pdf

Daggett, D. L., Hendricks, R. C., Walther, R., & Corporan, E. (2008). *Alternate Fuels for Use in Commercial Aircraft*. Retrieved from https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20080018472.pdf

Daiyan, R., Lu, X., Ng, Y. H., & Amal, R. (2017). Liquid Hydrocarbon Production from CO2: Recent Development in Metal-Based Electrocatalysis. *ChemSusChem*, *10*(22), 4342–4358. https://doi.org/10.1002/cssc.201701631

Davis, S. J., Caldeira, K., & Matthews, H. D. (2010). *Energy Infrastructure*. *243116*(September), 1330–1334.

Delpierre, M. (2019). *Ex-ante LCA study of wind-based hydrogen production in the Netherlands.* Leiden University; Delft University of Technology.

Ecochain. (2019). ecoinvent - Life Cycle Inventory - Databases - Ecochain. Retrieved November 9, 2019, from https://ecochain.com/databases/ecoinvent/

Fernández-Dacosta, C., Shen, L., Schakel, W., Ramirez, A., & Kramer, G. J. (2019). Potential and challenges of low-carbon energy options: Comparative assessment of alternative fuels for the transport sector. *Applied Energy*, *236*, 590–606. https://doi.org/10.1016/j.apenergy.2018.11.055

Heijungs, R., & Sun, S. (2002). The computational structure of life cycle assessment. *The International Journal of Life Cycle Assessment*, *7*(5), 314–314. https://doi.org/10.1007/bf02978899

Höjer, M., Ahlroth, S., Dreborg, K. H., Ekvall, T., Finnveden, G., Hjelm, O., … Palm, V. (2008). Scenarios in selected tools for environmental systems analysis. *Journal of Cleaner Production*, *16*(18), 1958–1970. https://doi.org/10.1016/j.jclepro.2008.01.008

Holladay, J. D., Hu, J., King, D. L., & Wang, Y. (2009). An overview of hydrogen production technologies.

Catalysis Today, *139*(4), 244–260. https://doi.org/10.1016/j.cattod.2008.08.039

Kätelhön, A., Meys, R., Deutz, S., Suh, S., & Bardow, A. (n.d.). *Climate change mitigation potential of carbon capture and utilization in the chemical industry*. https://doi.org/10.1073/pnas.1821029116

Keith, D. W., Holmes, G., St. Angelo, D., & Heidel, K. (2018). A Process for Capturing CO2 from the Atmosphere. *Joule*, *2*(8), 1573–1594. https://doi.org/10.1016/j.joule.2018.05.006

Kraan, O., Kramer, G. J., Haigh, M., & Laurens, C. (2019). An Energy Transition That Relies Only on Technology Leads to a Bet on Solar Fuels. *Joule*, 1–4. https://doi.org/10.1016/j.joule.2019.07.029

Lücking, L. . (2017). Methanol Production from Syngas. *Delft University of Technology*, 113.

Mac Dowell, N., Fennell, P. S., Shah, N., & Maitland, G. C. (2017). The role of CO2 capture and utilization in mitigating climate change. *Nature Publishing Group*, *7*. https://doi.org/10.1038/NCLIMATE3231

Maroto-Valer, M. M., Song, C., & Soong, Y. (2002). *Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century*. New York: Springer US.

McDaniel, N. D., & Bernhard, S. (2010). Solar fuels: thermodynamics, candidates, tactics, and figures of merit. *The Royal Society of Chemistry*, *Dalton Transactions*(39), 10021–10030. Retrieved from https://pubs.rsc.org/en/content/articlepdf/2010/dt/c0dt00454e

Mendoza Beltran, A., Cox, B., Mutel, C., van Vuuren, D. P., Font Vivanco, D., Deetman, S., … Tukker, A. (2018). When the Background Matters: Using Scenarios from Integrated Assessment Models in Prospective Life Cycle Assessment. *Journal of Industrial Ecology*, *00*(0), 1–16. https://doi.org/10.1111/jiec.12825

Miller, S. A., & Keoleian, G. A. (2015). Framework for analyzing transformative technologies in life cycle assessment. *Environmental Science and Technology*, *49*(5), 3067–3075. https://doi.org/10.1021/es505217a

Olah, G. A. (2005). Beyond Oil and Gas: The Methanol Economy. *Angewandte Chemie International Edition*, *44*(18), 2636–2639. https://doi.org/10.1002/anie.200462121

Ritchey, T. (2011). Modeling Alternative Futures with General Morphological Analysis. *World Futures Review*, *3*(1), 83–94. https://doi.org/10.1177/194675671100300105

Rogelj, J., D. Shindell, K. Jiang, S. Fifita, P. Forster, V. Ginzburg, C. Handa, H. Kheshgi, S. Kobayashi, E. Kriegler, L. M., & R. Séférian, and M. V. V. (2018). *Mitigation Pathways Compatible with 1.5°C in the Context of Sustainable Development. In: Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty*. Retrieved from https://www.ipcc.ch/site/assets/uploads/sites/2/2019/05/SR15_Chapter2_Low_Res.pdf

Sandalow, D., Friedmann, J., & McCormick, C. (2018). *ICEF DAC Roadmap*. Retrieved from https://www.icef-forum.org/pdf2018/roadmap/ICEF2018_Roadmap_Draft_for_Comment_20181012.pdf

The Carbon Capture & Storage Association (CCSA). (2019). Capture. Retrieved September 29, 2019, from http://www.ccsassociation.org/what-is-ccs/capture/

Torri, V. (2019). *MSc. Thesis*.

Trieb, F., Moser, M., & Kern, J. (2018). Liquid Solar Fuel – Liquid hydrocarbons from solar energy and biomass. *Energy*, *153*, 1–11. https://doi.org/10.1016/j.energy.2018.04.027

U.S. Energy Information Administration. (2016). International Energy Outlook 2016. In *International Energy Outlook 2016*. https://doi.org/www.eia.gov/forecasts/ieo/pdf/0484(2016).pdf

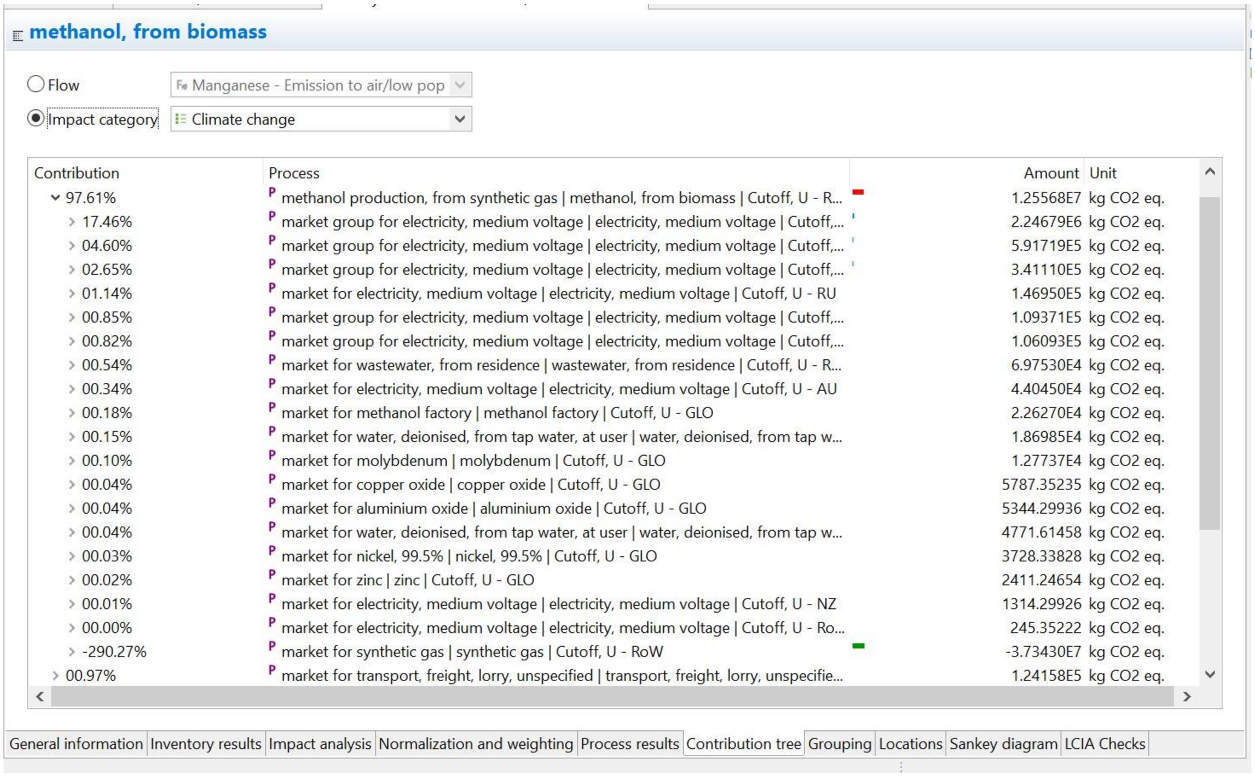
Van Der Giesen, C., Kleijn, R., & Kramer, G. J. (2014). Energy and climate impacts of producing synthetic hydrocarbon fuels from CO 2. *Environmental Science and Technology*, *48*(12), 7111–7121. https://doi.org/10.1021/es500191g

Van Geuns, L. (2019). *Fossil fuels: Preparing for an unpredictable future*. Leiden.

Appendix C – Discrepancies in contributions of the ecoinvent processes

As explained in section 5.2.6, the contributions in climate change results of biomethanol and resource depletion (water) results of fossil methanol, do not add up to 100%. This is illustrated in the graphs below.

C1 – process contribution results from ILCD impact assessment method



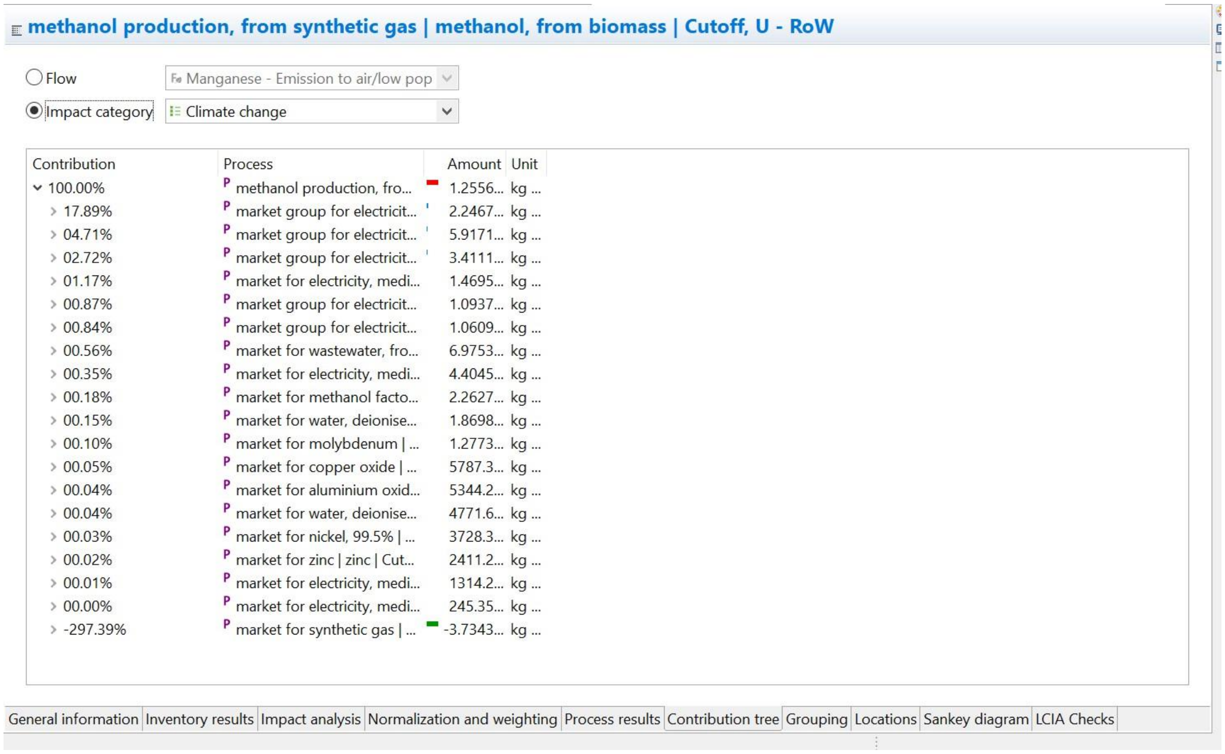
methanol, from biomass

○ Flow: Manganese - Emission to air/low pop

● Impact category: Climate change

Contribution	Process	Amount	Unit
97.61%	methanol production, from synthetic gas | methanol, from biomass | Cutoff, U - R...	1.25568E7	kg CO2 eq.
17.46%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	2.24679E6	kg CO2 eq.
04.60%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	5.91719E5	kg CO2 eq.
02.65%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	3.41110E5	kg CO2 eq.
01.14%	market for electricity, medium voltage | electricity, medium voltage | Cutoff, U - RU	1.46950E5	kg CO2 eq.
00.85%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	1.09371E5	kg CO2 eq.
00.82%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	1.06093E5	kg CO2 eq.
00.54%	market for wastewater, from residence | wastewater, from residence | Cutoff, U - R...	6.97530E4	kg CO2 eq.
00.34%	market for electricity, medium voltage | electricity, medium voltage | Cutoff, U - AU	4.40450E4	kg CO2 eq.
00.18%	market for methanol factory | methanol factory | Cutoff, U - GLO	2.26270E4	kg CO2 eq.
00.15%	market for water, deionised, from tap water, at user | water, deionised, from tap w...	1.86985E4	kg CO2 eq.
00.10%	market for molybdenum | molybdenum | Cutoff, U - GLO	1.27737E4	kg CO2 eq.
00.04%	market for copper oxide | copper oxide | Cutoff, U - GLO	5787.35235	kg CO2 eq.
00.04%	market for aluminium oxide | aluminium oxide | Cutoff, U - GLO	5344.29936	kg CO2 eq.
00.04%	market for water, deionised, from tap water, at user | water, deionised, from tap w...	4771.61458	kg CO2 eq.
00.03%	market for nickel, 99.5% | nickel, 99.5% | Cutoff, U - GLO	3728.33828	kg CO2 eq.
00.02%	market for zinc | zinc | Cutoff, U - GLO	2411.24654	kg CO2 eq.
00.01%	market for electricity, medium voltage | electricity, medium voltage | Cutoff, U - NZ	1314.29926	kg CO2 eq.
00.00%	market for electricity, medium voltage | electricity, medium voltage | Cutoff, U - Ro...	245.35222	kg CO2 eq.
-290.27%	market for synthetic gas | synthetic gas | Cutoff, U - RoW	-3.73430E7	kg CO2 eq.
00.97%	market for transport, freight, lorry, unspecified | transport, freight, lorry, unspecifie...	1.24158E5	kg CO2 eq.

Figure C.1: Discrepancies of ecoinvent's 'methanol, from biomass', used as alternative 2.



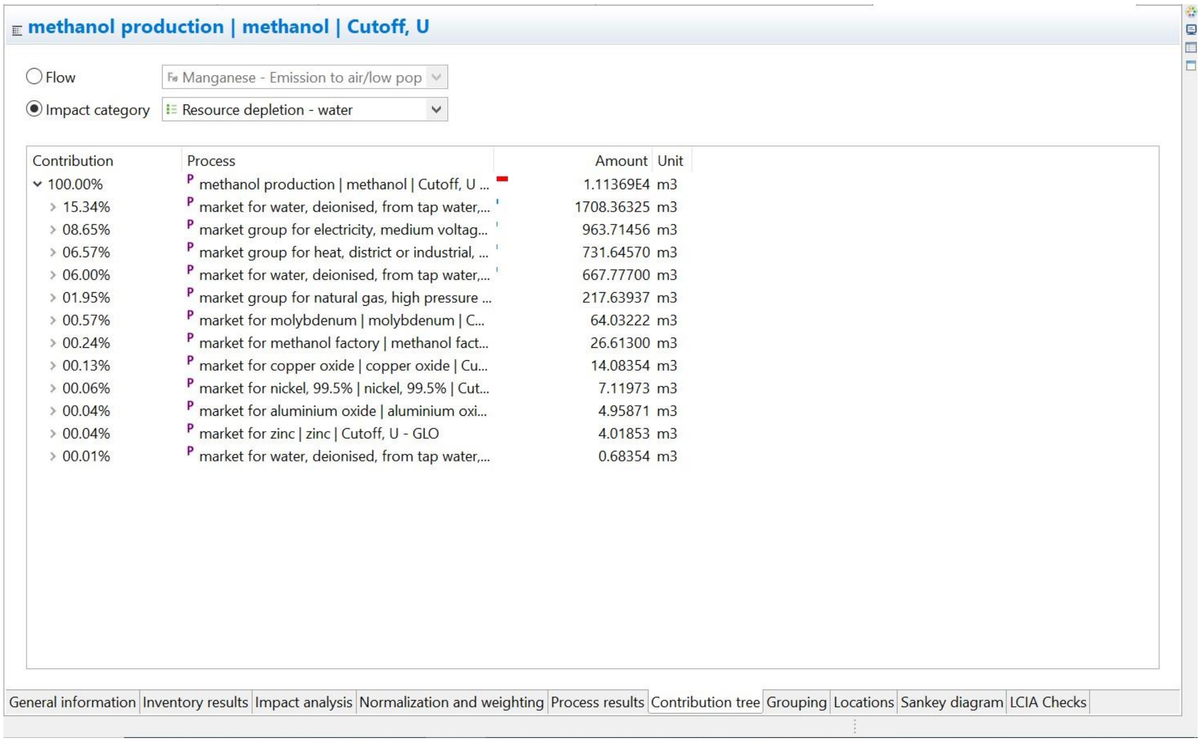
methanol production, from synthetic gas | methanol, from biomass | Cutoff, U - RoW

○ Flow: Manganese - Emission to air/low pop

● Impact category: Climate change

Contribution	Process	Amount	Unit
100.00%	methanol production, fro...	1.2556...	kg ...
17.89%	market group for electricit...	2.2467...	kg ...
04.71%	market group for electricit...	5.9171...	kg ...
02.72%	market group for electricit...	3.4111...	kg ...
01.17%	market for electricity, medi...	1.4695...	kg ...
00.87%	market group for electricit...	1.0937...	kg ...
00.84%	market group for electricit...	1.0609...	kg ...
00.56%	market for wastewater, fro...	6.9753...	kg ...
00.35%	market for electricity, medi...	4.4045...	kg ...
00.18%	market for methanol facto...	2.2627...	kg ...
00.15%	market for water, deionise...	1.8698...	kg ...
00.10%	market for molybdenum | ...	1.2773...	kg ...
00.05%	market for copper oxide | ...	5787.3...	kg ...
00.04%	market for aluminium oxid...	5344.2...	kg ...
00.04%	market for water, deionise...	4771.6...	kg ...
00.03%	market for nickel, 99.5% | ...	3728.3...	kg ...
00.02%	market for zinc | zinc | Cut...	2411.2...	kg ...
00.01%	market for electricity, medi...	1314.2...	kg ...
00.00%	market for electricity, medi...	245.35...	kg ...
-297.39%	market for synthetic gas | ...	-3.7343...	kg ...

Figure C.2: Same discrepancies identified in another source of biomethanol in ecoinvent, namely methanol from synthetic gas. The source of synthetic gas is wood chips.



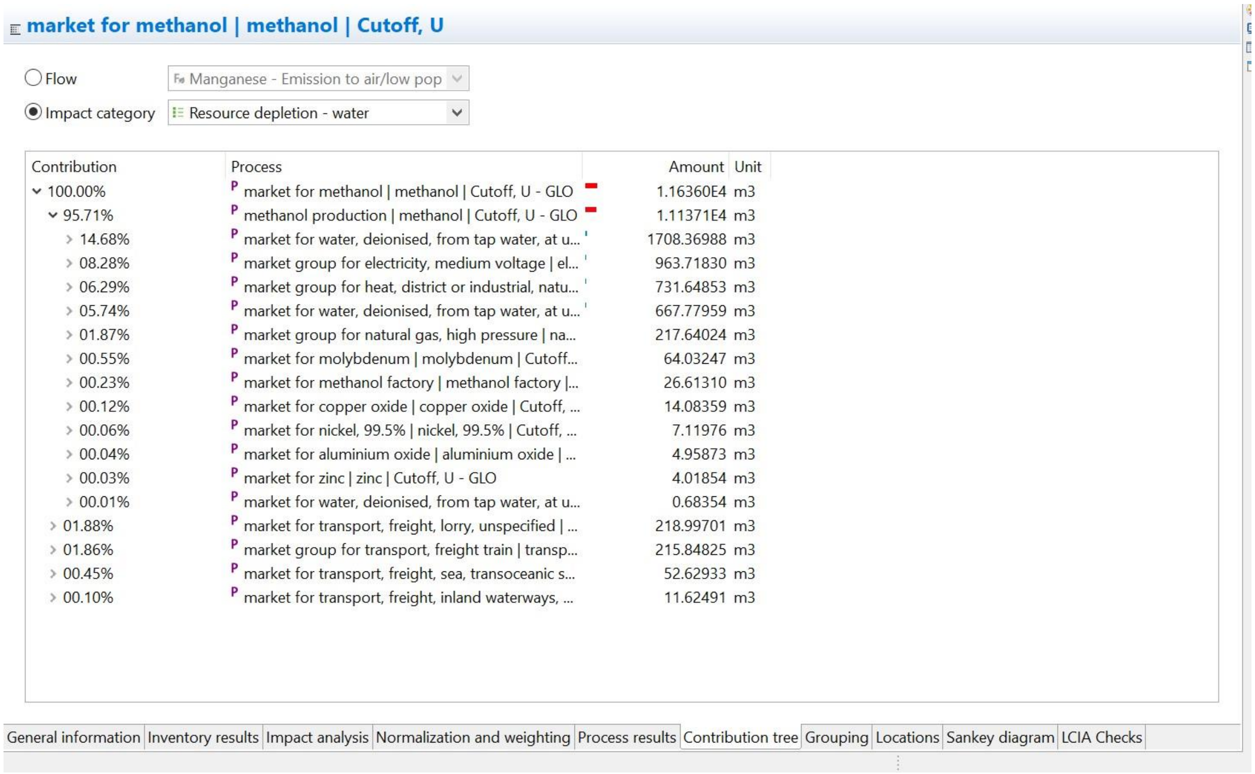
methanol production | methanol | Cutoff, U

○ Flow: Manganese - Emission to air/low pop

● Impact category: Resource depletion - water

Contribution	Process	Amount	Unit
100.00%	methanol production | methanol | Cutoff, U ...	1.11369E4	m3
15.34%	market for water, deionised, from tap water,...	1708.36325	m3
08.65%	market group for electricity, medium voltag...	963.71456	m3
06.57%	market group for heat, district or industrial, ...	731.64570	m3
06.00%	market for water, deionised, from tap water,...	667.77700	m3
01.95%	market group for natural gas, high pressure ...	217.63937	m3
00.57%	market for molybdenum | molybdenum | C...	64.03222	m3
00.24%	market for methanol factory | methanol fact...	26.61300	m3
00.13%	market for copper oxide | copper oxide | Cu...	14.08354	m3
00.06%	market for nickel, 99.5% | nickel, 99.5% | Cut...	7.11973	m3
00.04%	market for aluminium oxide | aluminium oxi...	4.95871	m3
00.04%	market for zinc | zinc | Cutoff, U - GLO	4.01853	m3
00.01%	market for water, deionised, from tap water,...	0.68354	m3

Figure C.3: Discrepancies in contribution analysis of methanol from fossil sources (alternative 3) from ecoinvent3.4. Approximately 60% of all impact is not shown.



market for methanol | methanol | Cutoff, U

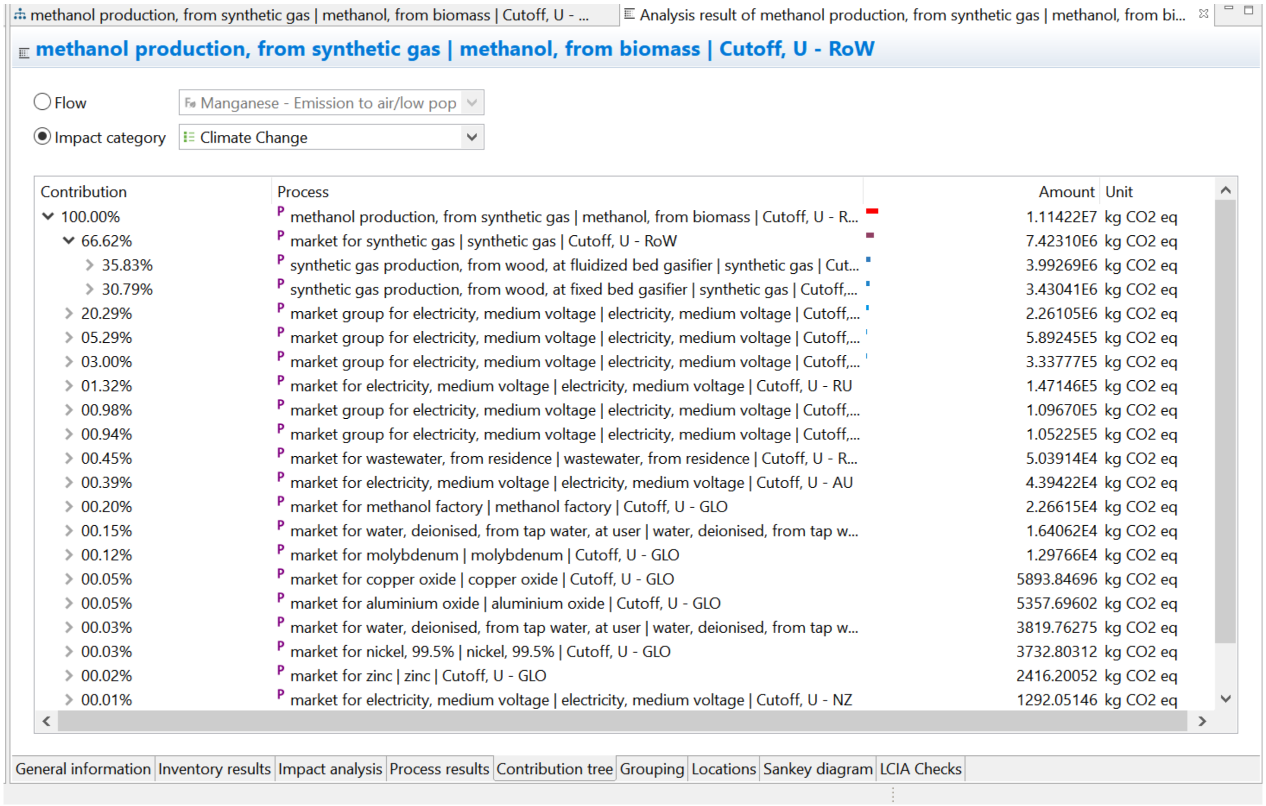
○ Flow: Manganese - Emission to air/low pop

● Impact category: Resource depletion - water

Contribution	Process	Amount	Unit
100.00%	market for methanol | methanol | Cutoff, U - GLO	1.16360E4	m3
95.71%	methanol production | methanol | Cutoff, U - GLO	1.11371E4	m3
14.68%	market for water, deionised, from tap water, at u...	1708.36988	m3
08.28%	market group for electricity, medium voltage | el...	963.71830	m3
06.29%	market group for heat, district or industrial, natu...	731.64853	m3
05.74%	market for water, deionised, from tap water, at u...	667.77959	m3
01.87%	market group for natural gas, high pressure | na...	217.64024	m3
00.55%	market for molybdenum | molybdenum | Cutoff...	64.03247	m3
00.23%	market for methanol factory | methanol factory |...	26.61310	m3
00.12%	market for copper oxide | copper oxide | Cutoff, ...	14.08359	m3
00.06%	market for nickel, 99.5% | nickel, 99.5% | Cutoff, ...	7.11976	m3
00.04%	market for aluminium oxide | aluminium oxide | ...	4.95873	m3
00.03%	market for zinc | zinc | Cutoff, U - GLO	4.01854	m3
00.01%	market for water, deionised, from tap water, at u...	0.68354	m3
01.88%	market for transport, freight, lorry, unspecified | ...	218.99701	m3
01.86%	market group for transport, freight train | transp...	215.84825	m3
00.45%	market for transport, freight, sea, transoceanic s...	52.62933	m3
00.10%	market for transport, freight, inland waterways, ...	11.62491	m3

Figure C.4: Alternative source of fossil methanol from ecoinvent shows the same issue - only a minor proportion of impact is demonstrated.

C2 – process contributions from ReCiPe



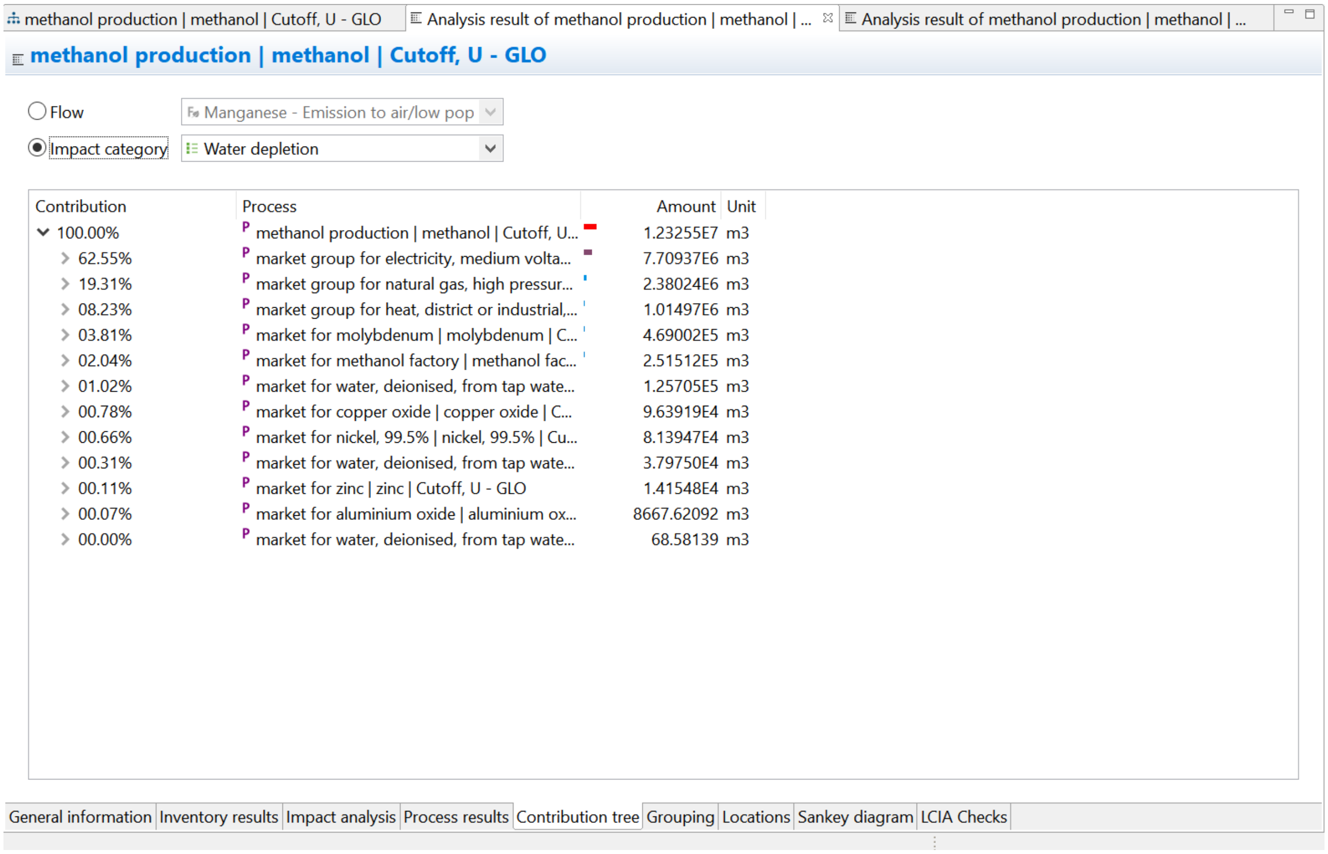
methanol production, from synthetic gas | methanol, from biomass | Cutoff, U - RoW

○ Flow Manganese - Emission to air/low pop

● Impact category Climate Change

Contribution	Process	Amount	Unit
100.00%	methanol production, from synthetic gas | methanol, from biomass | Cutoff, U - R...	1.11422E7	kg CO2 eq
66.62%	market for synthetic gas | synthetic gas | Cutoff, U - RoW	7.42310E6	kg CO2 eq
35.83%	synthetic gas production, from wood, at fluidized bed gasifier | synthetic gas | Cut...	3.99269E6	kg CO2 eq
30.79%	synthetic gas production, from wood, at fixed bed gasifier | synthetic gas | Cutoff,...	3.43041E6	kg CO2 eq
20.29%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	2.26105E6	kg CO2 eq
05.29%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	5.89245E5	kg CO2 eq
03.00%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	3.33777E5	kg CO2 eq
01.32%	market for electricity, medium voltage | electricity, medium voltage | Cutoff, U - RU	1.47146E5	kg CO2 eq
00.98%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	1.09670E5	kg CO2 eq
00.94%	market group for electricity, medium voltage | electricity, medium voltage | Cutoff,...	1.05225E5	kg CO2 eq
00.45%	market for wastewater, from residence | wastewater, from residence | Cutoff, U - R...	5.03914E4	kg CO2 eq
00.39%	market for electricity, medium voltage | electricity, medium voltage | Cutoff, U - AU	4.39422E4	kg CO2 eq
00.20%	market for methanol factory | methanol factory | Cutoff, U - GLO	2.26615E4	kg CO2 eq
00.15%	market for water, deionised, from tap water, at user | water, deionised, from tap w...	1.64062E4	kg CO2 eq
00.12%	market for molybdenum | molybdenum | Cutoff, U - GLO	1.29766E4	kg CO2 eq
00.05%	market for copper oxide | copper oxide | Cutoff, U - GLO	5893.84696	kg CO2 eq
00.05%	market for aluminium oxide | aluminium oxide | Cutoff, U - GLO	5357.69602	kg CO2 eq
00.03%	market for water, deionised, from tap water, at user | water, deionised, from tap w...	3819.76275	kg CO2 eq
00.03%	market for nickel, 99.5% | nickel, 99.5% | Cutoff, U - GLO	3732.80312	kg CO2 eq
00.02%	market for zinc | zinc | Cutoff, U - GLO	2416.20052	kg CO2 eq
00.01%	market for electricity, medium voltage | electricity, medium voltage | Cutoff, U - NZ	1292.05146	kg CO2 eq

Figure C.5: Contribution results of methanol from biomass assessed by ReCiPe impact assessment method. Here, all the percentage contributions add up to 100%, but no biogenic carbon is recorded.



methanol production | methanol | Cutoff, U - GLO
Analysis result of methanol production | methanol | ...
Analysis result of methanol production | methanol | ...

methanol production | methanol | Cutoff, U - GLO

○ Flow — Manganese - Emission to air/low pop

● Impact category — Water depletion

Contribution	Process	Amount	Unit
100.00%	methanol production | methanol | Cutoff, U...	1.23255E7	m3
62.55%	market group for electricity, medium volta...	7.70937E6	m3
19.31%	market group for natural gas, high pressur...	2.38024E6	m3
08.23%	market group for heat, district or industrial,...	1.01497E6	m3
03.81%	market for molybdenum | molybdenum | C...	4.69002E5	m3
02.04%	market for methanol factory | methanol fac...	2.51512E5	m3
01.02%	market for water, deionised, from tap wate...	1.25705E5	m3
00.78%	market for copper oxide | copper oxide | C...	9.63919E4	m3
00.66%	market for nickel, 99.5% | nickel, 99.5% | Cu...	8.13947E4	m3
00.31%	market for water, deionised, from tap wate...	3.79750E4	m3
00.11%	market for zinc | zinc | Cutoff, U - GLO	1.41548E4	m3
00.07%	market for aluminium oxide | aluminium ox...	8667.62092	m3
00.00%	market for water, deionised, from tap wate...	68.58139	m3

Figure C.6: Process contributions for fossil methanol production, examined via ReCiPe impact assessment method. All the process contributions are shown.