



## RENEWABLE ELECTRICITY-BASED, CYCLIC AND ECONOMIC PRODUCTION OF FUEL

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### LITERATURE REVIEW OF EXISTING LCA AND TECHNO-ECONOMIC STUDIES ON COMPETITIVE TECHNOLOGIES AND FUELS PRODUCTION

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<b>SUMMARY</b>	
<b>Keywords</b>	Life Cycle Assessment, Technoeconomic Analysis, Fuel Production Pathways, Synthetic Fuels, Environmental Impact, Global Warming Potential
<b>Abstract</b>	<p>The project EcoFuel addresses the topic “Development of next generation renewable fuel technologies from CO<sub>2</sub> and renewable energy”. It will develop a novel thorough process chain that significantly improves the energy efficiency for production of synthetic fuel out of CO<sub>2</sub> and water using renewable energy. The sustainable approach of EcoFuel shall be assessed through a LCA and a TEA. This study serves as the baseline for the evaluation, by analysing and determining environmental and economic aspects various production pathways of fossil, bio-based, and in particular synthetic fuels. Apart from the GWP of the different fuel pathways, further environmental impacts are discussed as well. Mean values, bandwidth, and uncertainties are elaborated, as far as possible.</p> <p>The technoeconomic analysis section of this report is a comparative discussion of process routes from CO<sub>2</sub> to hydrocarbon fuels such as gasoline, kerosene and diesel (i.e. “drop in” fuels). Several technoeconomic assessments are reviewed comparing promising processes covering a wide range of TRLs, with a focus on routes involving electrolysis. A separate discussion of the technoeconomic merits of different CO<sub>2</sub> capture methods is included, as is a discussion of which CO<sub>2</sub> reduction products are themselves most economically feasible to target.</p>
<b>Public abstract for confidential deliverables</b>	

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## 1 LIST OF ABBREVIATIONS

AAF	Aviation Alternative Fuel
CAPEX	Capital Expenditure Cost
CfD	Contracts for Difference
CORSIA	Carbon Offsetting and Reduction Scheme for International Aviation
DCS	Data Collection System
EEA	European Environment Agency
ESR	Effort Sharing Regulation
ETD	Energy Taxation Directive
ETS	Emission Trading System
EU MRV	EU Monitoring, Reporting and Verification
FQD	Fuel Quality Directive
GHG	Greenhouse Gas
ICAO	International Civil Aviation Organization
IMO	International Maritime Organization
LNG	Liquified Natural Gas
OPEX	Operating Expenditure Cost
OPS	Onshore Power Supply
PtL	Power-to-Liquid
RED	Renewable Energy Directive
RFNBO	Renewable Fuels of Non-Biological Origin
SAF	Sustainable Aviation Fuel
ZLEV	Zero- and Low-Emission Vehicle

## 2 INTRODUCTION

Despite the development efforts undertaken in the last decades in the transport sector, it is still a major contributor to several environmental impacts, particularly including climate change. The transport sector was not able to lower the overall CO<sub>2</sub> emissions, as the improvements in efficiency and reduction of engine and tailpipe emissions achieved by engine and vehicle manufacturers were used up by the increased number of vehicles, increased mileage driven, and further parameters like vehicle weight. The increased activities apply especially to the segments on-road transport, maritime and aviation.

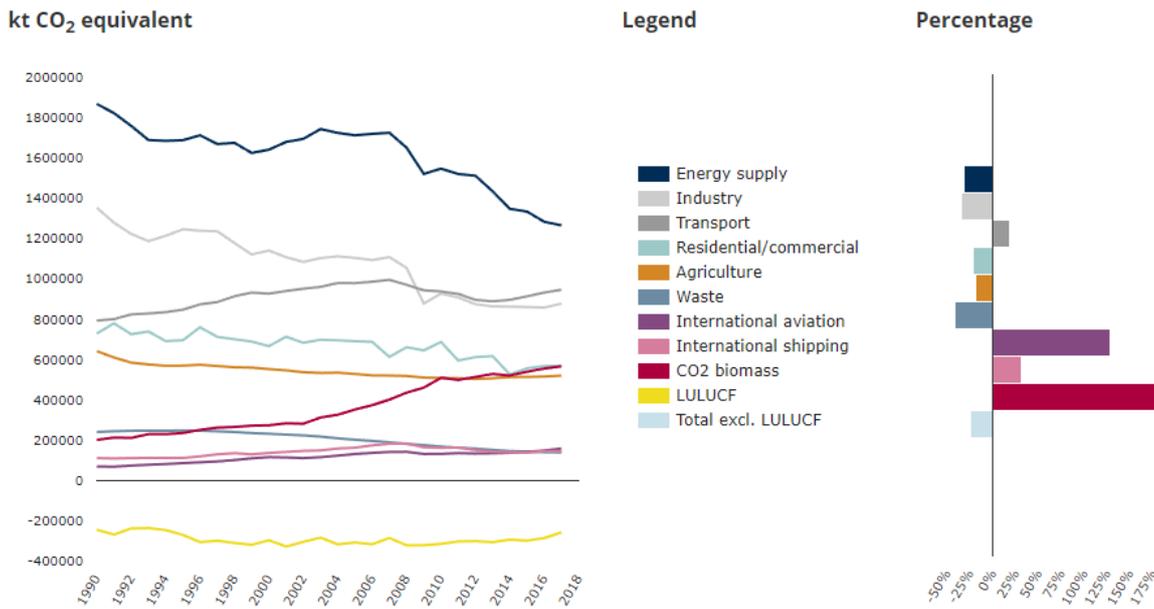


Figure 1: Development of CO<sub>2</sub>eq emissions per sector 1990 – 2018 [1]



Figure 2: Projections of Mobility Demand per Sector [2]

Being aware of these developments, the EU has set challenging targets to lower CO<sub>2</sub> emissions in the attempt to limit global warming. While some segments are easier to transform to zero-emission tailpipe propulsion technologies (e.g. urban battery electric vehicles), especially the segments mentioned are posing significantly more challenges due to the requirements of on-board energy storage requirements and re-fueling resp. re-charging infrastructure.

These challenges, together with the typical long-term operation phase of 15 to 50 years due to their main application, result in the necessity to offer alternative fuels as substitutes to the currently used fossil fuels especially, for heavy duty long-haul trucks, maritime vessels and airplanes. This is even more, as the operation phase (the use phase) has a predominant influence on the vehicle's entire life cycle emissions.

This study was performed in the course of the Horizon 2020 project 'Renewable Electricity-based, cyclic and economic production of Fuel (here referred to as 'ECOfuel'), responding to the call 'Building a Low-carbon, Climate Resilient Future: Secure, Clean, and Efficient Energy', topic LC-SC3-RES-26-2020. The literature review and analysis work were conducted in the second half year 2021 and reflect the latest status presented in publications and research papers.



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Development is on-going especially on alternative fuels (bio-based and synthetic), the progress, particularly regarding efficiency and TRL, will be monitored throughout the project, findings will be updated and reflected in the final report on the ecological and economic impacts of EcoFuel.

Deliverable D7.1 consists of three parts. Current interactions and impacts from legislation on fuel pathways are elaborated in the first part of the report, but only considered as far as defined at the time of preparation of this report and will have to be monitored closely, as changes are to be expected in the upcoming years. Still, the development effort, like the investments in production utilities for alternative fuels, will strongly be influenced by legislative regulations. Part A treats the environmental impact of fossil, bio-based and synthetic fuel production pathways, Part B deals with the techno-economic analysis, particularly of synthetic fuels, to provide a baseline to compare the EcoFuel process chain at the end of the project.



### 3 LEGISLATIVE REGULATIONS

The EU has committed to achieve 100% climate neutrality by 2050. On 11 December 2019, the Commission presented for that reason the European Green Deal. This is the new growth strategy of the EU, which aims to transform Europe into a climate-neutral, resource-efficient, and competitive economy with a modern, resource-efficient, and competitive society.

With the European Climate Law, which entered into force on June 20, 2021, the European Union committed to climate neutrality and to reducing greenhouse gas (GHG) emissions by at least 55% by 2030 in comparison with 1990 levels.

This chapter will give an overview, of which directives are for our scope of study relevant. It will describe all necessary legislative regulations which are important for the economic and ecological side important. Furthermore, it will be described, what will change with the newly presented Fit For 55 package, what problems are addressed and how these problems will be solved.

#### 3.1 RED II

RED II (Renewable Energy Directive II) is relatively new. It was introduced with the Clean Energy Package in 2019, its transposition deadline was past two weeks before the Commission presented the Fit For 55 package on 14 July 2021.

By 2030, the EU has raised its target for the consumption of Renewable Energy Sources to 32%, as outlined in RED II. Unlike the Commission's original proposal, the final agreement includes a transport sub-target. By 2030, Member States must require fuel suppliers to provide a minimum of 14% of the energy consumed in road transport and rail transport to be renewable. As in Article 2 Z 1 defined is "energy from renewable sources" or "renewable energy" is energy from renewable non-fossil sources, namely wind, solar (solar thermal and solar photovoltaic) and geothermal energy, ambient energy, tide, wave and other ocean energy, hydropower, biomass, landfill gas, sewage treatment plant gas, and biogas" [3]. For each country, the Directive 2009/28/EC specifies national targets for renewable energy for 2020, taking into account its starting point and overall potential. From a low of 10% in Malta to a high of 49% in Sweden, these targets differ greatly [4].

##### 3.1.1 Sustainability Criteria

In RED II, sustainability and GHG emission criteria are defined that bioliquids in transport must fulfill in order to count toward the overall 14 percent target and to qualify for financial support from public authorities. A few of these criteria are unchanged from the original RED, while others are new or reformulated. The RED II introduces sustainability criteria for forestry feedstocks as well as GHG criteria for solid and gaseous biomass fuels.

In Annex V (for liquid biofuels) and Annex VI (for solid and gaseous biomass for power and heat production) RED II are default GHG emission values and calculation rules described. An update or revision of the default values of GHG emissions from the Commission can be decided when technological development makes it necessary.

Greenhouse Gas savings thresholds in RED II for MS are:

After January 2021 65% transport biofuels, 70% transport renewable fuels of non-biological origin, 70 % Electricity, heating and cooling

After January 2026 65% Transport biofuels, 70% Transport renewable fuels of non-biological origin, 80% Electricity, heating and cooling.

To meet its EU GHG reduction targets biofuels play an important role. Biofuel production mostly takes place on cropland that was used for other agriculture before such as growing food or feed.

RED II defines Biofuels as “liquid fuel for transport produced from biomass” [4].

This agricultural production is still necessary, it may lead to the extension of agricultural land into non-cropland and there is a chance of including areas with high carbon stock like forests, wetlands and peatland – which is better known as indirect land use change (ILUC).

This can lead to the release of CO<sub>2</sub> which is stored in trees and soil and risks the saved GHG that results from increased biofuels to negate. In the Clean Energy for All Europeans package, the revised RED II introduces a new approach to address this issue of ILUC. Therefore, biofuels, bioliquids, and biomass fuels should with a significant expansion in land with high carbon stock should be limited. When calculating the share of renewable energy in transport and the overall national share of renewable energy, these limits will limit the amounts that the Member States may use when they calculate their national targets. It is still possible for member states to use (and import) fuels covered by these limits, but they cannot include these volumes when calculating whether they have met their renewable energy targets. The limits will gradually decline from 2023 to zero by 2030. An exemption from the directive is foreseen for biofuels, bioliquids and biomass fuels, which are certified as low ILUC-risk. [4].

### 3.1.2 Advanced Biofuels

Advanced Biofuels means in RED “biofuels that are produced from the feedstock listed in Part A of Annex IX” [4]. The transport sub-target of 14% is a dedicated target for advanced biofuels. As a share of the final consumption of energy in the transport sector of the contributed advanced biofuels and biogas should be 0,2% in 2022, 1% in 2025 and 3,5% in 2030 [3]. Member States can exempt fuel supplies which are supply fuel of electricity or renewable liquid and gaseous transport fuels of non-biological origin from the requirement to comply with the minimum share of advanced biofuels and biogas.

Feedstocks for the production of biogas for transport and advanced biofuels, may be considered twice their energy content.

The share of biofuels, bioliquids and biomass fuels should not be more than one percent higher than the share of such fuels in the final consumption of energy in the road and rail transport sectors. It is set with a maximum of 7% of the final consumption of energy in the road and rail transport in that Member state. The use of road vehicles will count 4 times its energy content towards the 14% renewable energy in transport target and 1.5 times when rail transport is used. Aviation and maritime fuels can opt in to contribute to the 14% transport target but are not obligated subject. In these sectors, the contribution of non-food renewable fuels will count as 1.2 times their energy content.

### 3.1.3 Voluntary schemes and national certification schemes

National and voluntary certification schemes in EU countries contribute to the sustainability of biofuels, bioliquids, and biomass fuels. The schemes verify and check compliance with the EU sustainability criteria. In addition, they verify that the production of feedstock for these fuels does not take place on land with high biodiversity and that land with high carbon levels has not been converted for biofuel, bioliquid, and biomass fuel production. Additional aspects of sustainability such as soil, water, air, and social criteria are included in some schemes. A third party verifies the whole production chain from the farmer growing the feedstock to the biofuel producer or trader during the certification process. Although the schemes are privately run, the European Commission recognizes them as valid. The Commission can recognize a voluntary scheme for up to five years. Under the recast of RED 2, the European Commission has not yet recognized voluntary schemes or national certification schemes of EU countries. [5]



### 3.2 Fuel Quality Directive (FQD)

The EU has to meet strict quality requirements for fuels in road transport to protect humans, health, the environment and make sure that vehicles travel safely from one country to another. The Fuel Quality Directive applies to petrol, diesel and biofuels used in road-transport as well as gasoil used in non-road mobile machinery. The directive requires a reduction of the GHG intensity of transport fuels by a minimum of 6% after 2020. The obligation for monitoring and reporting remains applicable after that date. RED II and FQD regulate the sustainability of biofuels and set out requirements. [6] “With effect from 1 January 2017, the GHG emission saving from the use of biofuels taken into account for the purposes referred to in paragraph 1 shall be at least 50 %. From 1 January 2018 that GHG emissions saving shall be at least 60 % for biofuels produced in installations in which production has started on or after 1 January 2017”. [6]

### 3.3 CO<sub>2</sub> emission performance standards for cars and vans

Passenger Cars and vans (light commercial vehicles) are collectively responsible for around 15% of total EU emissions of CO<sub>2</sub>. By January 2020 the regulation entered into force, which is setting CO<sub>2</sub> emission performance standards for new passenger cars and vans and sets EU fleet-wide CO<sub>2</sub> emission targets which apply from 2020, 2025 and 2030. Additionally, it includes a mechanism to incentivise the uptake of zero- and low-emission vehicles. The term "zero- and low-emission vehicle" refers to a vehicle with emissions between zero and 50 grams of CO<sub>2</sub>/km. This definition is technologically neutral because it pertains to the performance of the vehicles concerned and not to particular vehicle technology. A zero-tailpipe emission vehicle includes battery electric vehicles and fuel cell vehicles, as well as other vehicles with a low tailpipe emission like plug-in hybrid vehicles that have enough range to generate no emissions. As the metric for defining low emission vehicles is CO<sub>2</sub> emissions per km, there is also a direct link with CO<sub>2</sub> targets, which are expressed in the same way. By setting the threshold at 50 g CO<sub>2</sub>/km while taking into account the actual specific emissions of the vehicles, zero-emission vehicles, as well as low-emission cars with a longer zero-emission range, are particularly favored. Since the new target started applying in 2020, the average CO<sub>2</sub> emissions from new passenger cars registered in Europe have decreased by 12% compared to the previous year and the share of electric cars tripled. From 1 January 2030, the following EU fleet-wide targets will apply: a 37,5 % reduction of the target for new passenger cars in 2021, a 31 % reduction for new light commercial vehicles. The zero and low-emission vehicle benchmark shall apply from 1 January 2025 to a share of 15 % of the respective fleets of new passenger cars and new light commercial vehicles, and from January 2030 to a share of 35 % of the fleet of new passenger cars, and a share of 30 % of the fleet of new light commercial vehicles. [7]

A mechanism for zero-emission and low emission vehicles (ZLEV), which is a super credit system should apply to passenger cars with emissions of less than 50 g CO<sub>2</sub> /km (NEDC [New European Driving Cycle]). Vehicles are counted multiple times for the calculation of the average specific emissions of a manufacturer: 2 vehicles in 2020, 1,67 vehicles in 2021, 1,33 vehicles in 2022. A cap in the super-credits system is set at 7,5 g/km per car manufacturer over three years. This does not apply to vans. [7] [8]

### 3.4 Energy Taxation Directive

The ETD entered into force in 2003. Member States can introduce additional taxes for environmental purposes and under certain conditions exemptions or reduce tax levels. The mandatory exemptions refer to energy products used to produce electricity and for aviation and sea navigation fuel, while the optional exemptions concern electricity from renewables, for the transport of goods and passengers or for biofuels. In the ETD there is no link between the minimum tax rates of fuels and their energy content or environmental impact. Decarbonisation of transport and reduction of air pollutants are not taken into account. The directive is outdated. [9]



### 3.5 Emission Trading System (EU ETS)

In 2005 the European Emissions Trading Scheme (EU ETS) was introduced, with the goal to implement the Kyoto international climate protection agreement. It is the central European climate protection instrument. Norway, Iceland and Liechtenstein are also participants ETS (EU 30). Since 31.12.2020 the United Kingdom has also joined and is a member of the ETS-system. "The intra-European aviation has also been included in the EU ETS. In 2021 the system has also been linked to the Swiss emissions trading system." [10]

The ETS is working on a cap-and-trade system. A cap is set on the total amount of certain greenhouse gases that may be emitted by installations subject to emissions trading. All companies with large combustion plants with a capacity of more than 20 MW or production plants in energy-intensive industries are affected by European emissions trading. The member states issue a corresponding amount of emission allowances to the installations - partly free of charge, partly via auctions (one allowance permits the emission of one ton of carbon dioxide equivalent - CO<sub>2</sub>-eq). The emission allowances can be freely traded on the market (trade). This creates a price for the emission of greenhouse gases. This price creates incentives for the companies involved to reduce their greenhouse gas emissions. Over time, the cap will be reduced so that emissions fall. With the start of the fourth trading period in 2021, the framework conditions in the EU ETS have changed once again. [10]

### 3.6 FIT for 55

The Fit For 55 package, which was launched in July 2021, is a set of proposals to revise and update EU legislation. The EU seeks to reduce net GHG emissions by at least 55% by 2030. Additionally, it should put new initiatives in place with the aim of ensuring that EU policies are in line with the climate goals stated by the Council and the European Parliament.

#### 3.6.1 Proposal for a review of RED II targets

The new proposal of the RED II is part of the Fit For 55 package to deliver on the European Green Deal, therefore the Commission proposed several, mainly punctual changes to the RED II in order to pave the Union's road to climate neutrality by 2050.

The proposal aims to increase the target of 40% renewables in the EU's overall gross final energy consumption by 2030. The enhancement of sectorial sub-targets and measures across sectors with a particular focus on transport, buildings, and industry, all of which have been slower to integrate renewable energy to date. An adjusted scope for the production and use of green hydrogen. Strengthening the role of renewable PPAs (Power Purchase Agreement), which provides a complementary route to the market of renewable power generation in addition to support schemes by the Member States or to selling directly on the wholesale electricity market as well as guarantees of origin and introduction of a credit system allowing fuel suppliers to buy credits from suppliers of renewable electricity to public charging points for electric vehicles.

It should be established a mechanism by the member states to allow fuel suppliers in their territory to exchange credits for supplying renewable energy to the transport sector. Economic operators shall receive credits for supplying renewable electricity to electric vehicles through public recharging stations. Furthermore, there should be an update of sustainability criteria for bioenergy, including the cascading-principle for woody biomass. [11]

In the Explanatory memorandum is described that there is a need for EU action. In the development which is cost-efficient of sustainable renewable energy within a more integrated energy system cannot be sufficiently achieved by the Member States alone. There is a need for the right incentives to Member



States with different ambition levels to accelerate in a coordinated way, the energy transition from the traditional fossil fuel-based energy system towards to a more energy efficient system based on renewables-based generation.

To create a sufficient incentive to use biofuels and biogas produced from food and feed crops in transport, Member States should continue to be able to choose whether count them or not towards the transport target. “If they do not count them, they may reduce the greenhouse gas intensity reduction target accordingly, assuming that food and feed crop-based biofuels save 50% greenhouse gas emissions, which corresponds to the typical values set out in an annex to this Directive for the greenhouse gas emission savings of the most relevant production pathways of food and feed crop-based biofuels as well as the minimum savings threshold applying to most installations producing such biofuels” [11].

The usage of multipliers are made unnecessary because the reduction target is expressed in greenhouse gas intensity. Renewable energy sources save different amounts of greenhouse gas emissions and therefore contribute another target. It should be considered that renewable electricity has zero emissions and to save 100% emissions compared to the electricity compared to electricity of fossil production. This will create an incentive for the use of renewable electricity. Renewable and recycled carbon fuels won't never achieve that high percentage of savings and therefore is electrification relying on renewable energy the most efficient way to decarbonise road transport. In maritime and aviation sectors, it is harder to electrify and there is appropriate to keep the multiplier for those fuels. [11]

Currently, the proposal follows the ordinary legislative procedure. Member states will have time to transpose the new rules into national law after its entry by the end of 2024 [12]

### 3.6.2 Fuel EU maritime

In terms of volume, EU external trade accounts for approximately 75% of the total and EU internal trade for 31%. Meanwhile, ship traffic to and from ports in the European Economic Area accounts for about 11% of total EU CO<sub>2</sub> emissions from transport, and 3-4% of total EU CO<sub>2</sub> emissions. The maritime sector is an important component of Europe's transport system and European economy.

In 2018 ships above 5 000 gross tons calling at EEA (European Environmental Agency), ports have to monitor and report fuel consumption, CO<sub>2</sub> emission and transport work per voyage on an annual basis. Since 2019 operates a global GHG data collection system (DCS) by the IMO. The two monitoring systems are not aligned yet. To reduce sulphur oxides (SO<sub>x</sub>), the EU adopted the already existing IMO limits, limits for maximum sulphur content in marine fuels in emission control areas into its law and make them legally binding.

In 2016 the IMO announced a global “sulphur cap”, after the availability of compliant fuels was confirmed in all waters from 2020. Ships can either install an exhaust cleaning system (scrubber) to use a low sulphur fuel or switch to LNG. This measure limits only SO<sub>x</sub>, it does not address GHG emissions from shipping. The RED ensures that the share of renewable energy within the final consumption of energy in the transport sector is a least 14% by 2030 and sets sub-targets for advanced biofuels.

FuelEU Maritime is a part of the Fit For 55 package and proposes to reduce the greenhouse gas intensity of the energy used onboard 75% by 2050 by promoting the use of greener fuels. Despite recent progress, the maritime sector still heavily relies on fossil fuels and emits lots of greenhouse gases and other harmful pollutants. The draft law is an initiative that proposes a common framework for regulation across the European Union (EU) designed to increase the share of renewable and low-carbon fuels in international maritime transport without creating barriers to the single market. A maximum limit for the GHG content of energy used by ships calling at European ports is to be set.

To meet future needs, the development and deployment of renewable and low-carbon fuels with high potential for sustainability, commercial maturity, and innovation potential should be encouraged. “Renewable fuels of non-biological origin” (RFNBO) means biomass fuels and biofuels as defined in Article



2, points (27) and (33) of Directive (EU) 2018/2001 and –synthetic and paraffinic fuels, including ammonia, produced from renewable energy” [13].

Sustainable maritime fuels are produced from feedstocks, which are listed in Parts A and B of Annex IX of RED II. Especially, sustainable maritime fuels produced from feedstock listed in Part B of Annex IX of RED II are essential, as currently the most commercially mature technology to decarbonize maritime transport already in the short term. The proposal aims to promote the use of low-carbon fuels by putting limits on the carbon intensity of energy used onboard ships and mandating onshore power supply (OPS) at EU ports. [13]

From 2020 to 2025, the GHG intensity of energy used onboard will be reduced by 2%. It is expected that over time, the requirements will become increasingly strict, with a 6 percent improvement expected in 2030 and a 75 percent cut expected in 2050. The above requirements would apply to all of the energy used onboard a ship between ports in the EU. However, they would only cover 50 % of the energy used by ships arriving at or departing from EU ports on voyages to third countries. Those updated fuel standards would apply to ships that use fuel from within the EU, as well as those that use fuel from outside the EU. As part of the proposal, a methodology and common standards for fuel monitoring, reporting, verification and accreditation are introduced. The new system would be separate from and complement the existing EU MRV system but should utilize the existing EU THETIS reporting database. Compliance certificates would be required for ships operating within the EU. As of January 2030, all freight and passenger ships staying in EU ports for longer than two hours are required to connect to the shore-side supply of electricity (OPS) and use this supply for all energy needs while at berth, unless they use a zero-emission technology or are in an emergency.

The fuel mix in the maritime sector relies entirely on fossil fuels as a result of insufficient incentives for operators to cut emissions as well as the lack of mature, affordable and globally utilizable technological alternatives to fossil fuels in the sector.

In the explanatory memorandum, there were several market failures described that partly cause and reinforce the problem, like interdependencies between supply, distribution and demand of fuels. Distortion of competition between ship operators and diversion of trade routes may pose obstacles to the single market since fuel expenses represent a substantial share of ship operators' costs.

Secondly lack of information on future regulatory requirements. By increasing the predictability in the regulatory framework, it is expected that technology development and fuel production will be stimulated and should be able to unlock the current chicken-and-egg dilemma (high fuel investment costs and big uncertainty for investors) between demand and supply of renewable and low-carbon fuels. Thirdly a long life span of assets (vessels and bunkering infrastructure), the possibility to bunker outside the EU, the IA recommended that the policy target fuels used on voyages to and from EU ports, rather than fuels sold in the EU. As the lack of demand for clean fuels was seen to be the main problem, the policy should target the demand side rather than the supply. The IA takes as its starting point the need to provide legal certainty, focus on the demand side to stimulate production and use renewable and low-carbon fuels while addressing the issue of carbon leakage.

Ships carrying freight and passengers must use shore-side power or similar zero-emission technology, regardless of the option chosen. The preferred option is option 3.

FuelEU maritime is a goal-based GHG intensity target that increases in stringency over time. To account for all the life cycle GHG emissions (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) Well-To-Wake CO<sub>2</sub>eq is used. T&E warns that the simple goal-based target would likely result in the acceleration of fossil natural uptake as the cheapest alternative fuel eligible until 2040 as well as biofuels from dubious origin. [14]



The proposed targets take only into account that ships reduce their energy GHG intensity by 2% until 2029, 6% until 2034 and 13% until 2039. The proposal aims only for a limit ambition in the first 15 years. Furthermore, the proposal does not consider the current market trends for the uptake of LNG in business as usual scenario "and implicitly counts of contribution of shoreside electricity implicitly counts the contribution of shoreside electricity (SSE or OPS) use at berth to the achievement of the overall GHG intensity improvements. For example, by 2025, natural market uptake and the implementation of the SSE mandate for passenger ships and containerships will contribute to a 0.9% reduction, or about half of the -2 percent target. Business as usual LNG and the SSE mandate will already achieve 2.9% reduction by 2030, which is half of the 6% target for 2030-2034

As a result, ships would use half as much alternative fuel as indicated by the headline targets. If shipping is to fully decarbonise by 2050, the -13% target for 2035-2039 means reducing their GHG intensity by 87% (i.e. switching the remaining 87% of their energy to sustainable alternatives).

In any case, this would be an unrealistic decarbonisation trajectory and result in higher cumulative emissions than is allowed under the remaining carbon budget. This clearly shows that FuelEU Maritime Regulation's ambition is not in line with the Paris Agreement's temperature goals and that the targets need to be revised upward, especially in the initial years of the regulation's implementation. [14] [15]

### 3.6.3 ReFuel EU

At global and EU levels some policy actions for supporting the use of sustainable aviation fuels (SAF) already exist, like the International Civil Aviation Organization (ICAO) carbon offsetting and reduction scheme for international aviation (CORSIA), which allows aircraft operators to use SAF that comply with a dedicated sustainability framework, instead of purchasing emissions offsets. The EU ETS, which provides an incentive for aircraft operators to use biomass-based SAF certified as compliant with the sustainability framework of RED II, by attributing them 'zero emissions' under the scheme; this means that airlines do not have to surrender any emissions allowances when SAF is used instead of fossil jet fuel.

According to RED II, Member States can count SAF towards the achievement of their national renewable energy targets, on the condition that they comply with the sustainability criteria listed in the directive. However, the Commission estimates that the regulatory framework for renewable energy and the EU ETS has not led to a sufficient increase in the uptake of SAF and that CORSIA on its own may not provide a sufficient economic incentive for airlines to increase the use of SAF.

The Fit For 55 package tabled in July 2021 rules on the conduct of investigations and the application of redressive measures in respect of practices distorting competition between EU and third-country air carriers. However, fuel tankering practices have so far not been addressed by EU rules. According to the Commission proposal, safeguards against fuel tankering are necessary because these practices undermine fair competition (in those certain aircraft operators are able to benefit from favorable aviation fuel prices at their home base), and can affect the attractiveness of certain airports. The Commission also suggests that eliminating tankering practices has significant environmental benefits, and points to a Eurocontrol study that estimates that 20% of the flights in Europe were operated using some fuel tankering, with a significant impact on emissions due to the heavier onboard weight of aircraft

The proposal introduces targets for sustainable aviation fuel (SAF) and synthetic fuels from 2025 to 2050. According to the ICAO there is a difference between aviation alternative fuels (AAF), which are obtained from sources other than petroleum, such as coal, natural gas, biomass, and hydrogenated fats and oils with the potential to be sustainably produced, and sustainable aviation fuels (SAF), which are AAF that meet sustainability criteria. It does not exist a single internationally agreed definition of SAF. Sustainability criteria for AAF have been stated under CORSIA – a market-based measure to limit greenhouse gas emissions from international aviation to their 2020 levels. [16]



RED, adopted in 2009 defined sustainability requirements for biofuels. RED II reinforced the sustainability criteria, entered into force at the end of 2018 and will need to be transposed into national law by the end of June 2021. Under CORSIA, concerning GHG, SAF should achieve a life cycle emission reduction of at least 10% compared to a fossil fuel baseline of 89 grams of CO<sub>2</sub> equivalent per megajoule (g CO<sub>2</sub>e/MJ). RED II states, to qualify biofuels as renewable energy sources, fuels have to achieve a 65 % greater reduction in emissions against a fossil fuel baseline of 94 g CO<sub>2</sub>e/MJ.

The calculation of the shares of SAF and synthetic aviation fuels is based on volume (difference to RED II, which is based on energy). [17]

ReFuel Eu knows three categories of SAF: So-called advanced biofuels, which are fuels that are produced from feedstock listed in Annex IX, Part A of the Renewable Energy Directive and Fuels produced from feedstock listed in Part B of the initiative Synthetic Aviation fuels. Synthetic fuels, e-fuels or Power-to-liquid (PtL) fuels are fuels made from renewable sources other than biomass, e.g. wind and solar power. As a basic explanation, renewable energy and water are used in an electrolysis to produce hydrogen, which is subsequently synthesized with CO<sub>2</sub> into syngas. The resulting syngas is then further processed into fuel. [17]

With the increasing shares of SAF in the aviation fuel mix pollutant emissions would be reduced (CO, NO<sub>x</sub> and PM) between 2030 and 2050.

The IA outlines the urge for action and lists several policy options, detailing the impact of the measures, including emissions reductions and projected costs.

The first set of policy options included a requirement for fuel suppliers to supply SAF at EU airports; the second set of options included a requirement for airlines to uptake SAF when flying from EU airports; and a third set, the preferred policy options set, included obligations on fuel suppliers to distribute SAF, and on airlines to uptake jet fuel before departing from EU airports.

Some policy options defined targets for the increased use of SAF in terms of volume, while others defined the targets in terms of CO<sub>2</sub> intensity reduction. [2]

Fundings are important in developing and upscaling SAF production and deployment. It will be necessary for substantial private and public investment in the years to reduce the gap between SAF prices and conventional jet fuel prices. This can happen by supporting CAPEX or OPEX costs of new industrial-scale SAF production sites, at least in the first stages while the price gap remains a market barrier. Public Funding from the Member States and the EU budget can help to support the instruments Horizon Europe, Connecting Europe Facility, InvestEU, NextGenerationEU, or Innovation Fund under the EU ETS.

ReFuel EU shall apply from January 2023, the reporting obligations shall apply from April 2024 for the reporting period 2023. The minimum share of SAF, including a minimum share of synthetic aviation fuel and the refueling obligation, should apply by January 2025. [16] [18]

### **3.6.4 Revision of CO<sub>2</sub> emission performance standards for cars and vans**

As part of the Fit for 55 legislative package, the European Commission is proposing to revise CO<sub>2</sub> emission performance standards for cars and vans to set more ambitious EU fleet-wide CO<sub>2</sub> emission reductions for new cars and vans from 2030 onward (55% by 2035 [compared to 2021] and a 100% reduction by 2050). Additionally, the Commission proposes to remove the incentive for zero- and low-emission vehicles from 2030 onwards. The mechanism of ZLEV would reduce planning certainty for automotive manufacturers and their suppliers, which could hinder the transition to zero-emission vehicles. It would be an incentive to direct fuels to road transport that will be needed to decarbonize sectors with fewer alternatives.

This would result in an inherent approach to fuels decarbonization sectors with fewer options, such as aviation and maritime. As a consequence, it would result in an incoherent approach to fuel decarbonization, while specific instruments are proposed for this purpose (the revision of the Renewable



Energy Directive, the Energy Taxation Directive, emissions trading for road transport, and fuel-specific initiatives in the aviation and maritime sectors). Furthermore, if a voluntary fuel crediting system is established between fuel suppliers and vehicle manufacturers, compliance costs for manufacturers would increase, which would impact the total cost of ownership.

E-fuels are not included because the EU sees it essential that e-fuel credits are not added. Otherwise, it would severely undermine the credibility of the CO<sub>2</sub> Standards, as it would open the possibility of double-counting emission reductions with other existing regulations, like FQD or RED II and would delay investments in electromobility. As a result, it would also end in an unenforceable regulation since carmakers have no control over what fuel is used in the cars they produce. Additionally, the EU sees no decarbonization solution for cars, as they will cost more than batteries even in 2030 and lead to more CO<sub>2</sub> emissions. Their limited availability must be reserved for sectors such as maritime and aviation, where it is harder to abate CO<sub>2</sub> emissions. [20] [21] [22]

### 3.6.5 Revision of the EU Emission Trading System (EU ETS)

As part of the "Fit for 55" package, the EU Commission will also submit further comprehensive proposals for adapting the EU ETS for the fourth trading period in July 2021 [23]. New targets of ETS for 2030 are emission reduction of at least -61% (previously -43%) and a new linear reduction factor of 4,2% cut to ETS emissions cap every year (if started in 2024) to achieve the 2030 target sharper reduction will be required in new sectors. The maritime sector will be included in the existing EU ETS. Road transport and buildings will be covered by a distinct separate ETS system and are supposed to start in 2025, with a cap on emissions set from 2026 [10] [23]. Fuel suppliers have to buy and trade emitting permits to meet their need without reaching the maximum cap without reaching the maximum cup, which will be reduced over time (43% in 2030 compared to 2005. 25%). To prevent high costs from fuel suppliers, the social climate fund is to be set up. Between 2025 and 2032, EU funds of 72.2 billion euros are to be made available to member states, where national governments are expected to top up to a total budget of 144.44 billion euros. A special mechanism is to be included in the ETS to control excessive increases in the carbon price. Furthermore, all new cars registered in the EU from 2035 onwards will be emission-free and thus internal combustion engines will be phased out.

With the proposal, the commission also reforms the EU ETS rules for aviation, which abolish some of their privileges and start to apply more effective price on aviation emissions. It will still continue to implement CORSIA despite its confirmed lack of economic and environmental integrity.

In the IA are several arguments that justifies the need for policy makers to go further than the current proposal:

Remove fee allowances and finance the deployment of e-fuels through the use of auction revenues.

Free allocations were implemented to counter the risk of carbon leakage, where production moves from the EU to third countries. However, the principle of carbon leakage does not apply to the aviation sector. The IA notes that "there is no evidence of carbon leakage at present for aviation, because there is equal treatment of all airlines on flight routes covered by the ETS" [24]. It explains that "a significant risk for carbon leakage for aviation due to the ETS has not been substantiated due to its very nature (difficulties or even impossibility to change/divert route due to the very nature of the traffic)" [24]. This "undermines the effectiveness of the carbon price "there is no evidence of carbon leakage at present for aviation, because there is equal treatment of all airlines on flight routes covered by the ETS" [24]. It explains that "a significant risk for carbon leakage for aviation due to the ETS has not been substantiated due to its very nature (difficulties or even impossibility to change/divert route due to the very nature of the traffic)". This "undermines the effectiveness of the carbon price. Additionally, the IA mentions the impact of COVID 19 on air traffic the level of 2019 won't reach before 2024. They would create downwards pressure on the

prices of ETS allowances. There is no reason to continue until 2027 and should phase out immediately. [25]

The revenues by stopping the free allowances could help finance contracts for difference (CfD) promoting and use of sustainable alternative fuels. The CfDs are agreements that are used to fill the gap between what it cost to produce and what the market is willing to pay. These agreements have been used to support novel alternative technologies such as renewable electricity (wind, solar). CfDs can be awarded through an auctioning process to the producer offering the lowest cost, therefore ensuring public money is put to the most efficient use.

Furthermore, reintegrate extra EU aviation emissions within the scope of EU ETS and limit the use of CORSIA in routes departing from Europe because there is a given risk of carbon leakage. The proposal fails to address the bulk of aviation emissions, which makes an amount of 60% of emissions, which take an extra price on extra EU-flights. CORSIA lacks of environmental integrity and is an existing threat to the existing climate commitments under the Paris Agreement. CORSIA is the main tool to regulate emissions on extra EU flights and is a cheap offsetting scheme that allows aviation emissions to grow. It includes credits that don't promote emission reductions and a risk of being double counted as well as mostly prices under 1€. The IA writes that additionality offset credits, with accounting, the policy options with wider ETS coverage provide more certainty of environmental effectiveness as the CORSIA's participation and their uncertainties. "The CORSIA's current aim of carbon neutral growth of international aviation emissions above 2020 levels, is not ambitious enough to deliver a significant contribution from the international aviation sector towards the Paris Agreement's global goal" [24]. Thirdly propose additional measures to strengthen EU ETS and address non -CO<sub>2</sub> emissions. [25]

The Effort Sharing Regulation (ESR) covers sectors outside the EU ETS, which establishes an overall EU-wide greenhouse an overall EU-wide greenhouse gas emission reductions target and binding annual targets for individual Member States to be achieved by 2030. Among others, the road transport and buildings sectors, as well as emissions from domestic navigation have together around 50 % of ESR emissions. The sectors which are covered by the ESR are not subject to an EU-wide carbon price signal. Additional incentives (through carbon pricing) are necessary to achieve cost-efficient emission reductions in buildings and road transport, the new ETS would complement the ESR. The scope of the current ESR maintains incentives and accountability for national action. The proposal will provide incentives by making free allocation conditional on investments in techniques to increase energy efficiency. In the IA, there is a focus primarily on aviation's contribution to the European climate target for 2030 and the impact of different options for including aviation emissions under the EU ETS versus CORSIA. It is considered the pace at which to increase auctioning of allowances and recommended an immediate phasing out of free allowances. [23]

### 3.6.6 Revision of the Energy Taxation Directive

The existing ETD focuses on internal objectives, while the revision focuses more on the environmental impact.

The new proposal has the goal to align the taxation of energy products with EU energy and climate policies, promoting clean technologies and removing outdated exemptions and want to reduce the current encouragement of the usage of fossil fuels.

With the proposal, fuels will start being taxed according to their energy content and environmental performance rather than their volume, the categorization of energy products for taxation purposes will get simplified to ensure that fuels that are the most harmful ones get taxed. Products that are covered by the Directive are grouped and ranked to their environmental performance, this means fuels that have the



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most negative impact on the environment will be subject to higher minimum rates. Furthermore, fossil fuels that are used for intra EU air transport, maritime transport and fishing won't be exempt from energy taxation anymore. New energy products like hydrogen will get recognized. The proposal includes measures that double taxation of stored electricity and a significant limitation on Member States exempting or reducing the rates applicable to energy products, processes and sectors shouldn't occur. Additionally, there should be an increase in minimum tax rates to reflect the current pricing and to keep the ETD up to date there should be a revision in five years-cycle. The proposed minimum rates should reflect the recent prices and will be automatically adjusted annually, based on the data of Eurostat. The previous minimum rates that were set in 2003 have never been updated to reflect the current prices. The proposal will enter into force by January 2023.

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## RENEWABLE ELECTRICITY-BASED, CYCLIC AND ECONOMIC PRODUCTION OF FUEL

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### ENVIRONMENTAL IMPACT OF FUEL PRODUCTION PATHWAYS

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<b>R</b>	Report	<b>X</b>
<b>P</b>	Prototype	
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<b>SUMMARY</b>	
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## 1 LIST OF ABBREVIATIONS

AAF	Aviation Alternative Fuels	LCA	Life Cycle Assessment
AEL	Alkaline electrolysis	LHV	Lower heating value
ALCA	Attributional LCA	LNG	Liquified Natural Gas
API	American Petroleum Institute	LPG	Liquified Petroleum Gas
BtL	Biomass to Liquid	LT-DAC	Low temperature direct air capture
CBM	Compressed Bio Methane	LTFT	Low temperature Fischer-Tropsch
CC	Carbon Capture	LUC	Land Use Change
CFF	Conventional Fossil Fuel	MDEA	N-methyl diethanolamine
CLCA	Consequential LCA	MJ	Mega Joule
CNG	Compressed Natural Gas	MtG	Methanol to gasoline
CRR	Continuous-regenerative reforming	OME	Oxymethylene dimethyl ether
CSP	Concentrated Solar Power	PBtL	Power and biomass to liquid
Ctg	Cradle to Gate	PEMEL	Proton exchange membrane electrolysis
CtG	Cradle to Grave	PPA	Power Purchase Agreement
CtL	Coal to Liquid	PSA	Pressure swing adsorption
DAC	Direct Air Capture	PtG	Power to Gas
DLUC	Direct Land Use Change	PtL	Power to Liquid
DME	Dimethyl Ether	REA	Rapid Evidence Assessment
DMM	Dimethoxymethane	RED	Renewable Energy Directive
DTL	Direct thermal liquification	rWGSR	reverse water-gas shift reaction
EoL	End of life	SAF	Sustainable Aviation Fuel
ER	Equivalence ratio	SB	Steam to biomass
FAME	Fatty Acid Methyl Ester	SMR	Steam Methane Reforming
FFA	Free Fatty Acid	SNG	Synthetic Natural Gas
FPPW	Fuel Production Pathway	SOEL	Solid oxide electrolysis
FT	Fischer-Tropsch	SRF	Short rotation forestry
GHG	Greenhouse Gas	SRR	Semi-regenerative reforming
Gtg	Gate to Gate	TDS	Total dissolved solids
gtG	Gate to Grave	TMP	Trimethylpentane
GtL	Gas to Liquid	TSA	Temperature swing adsorption
GWP	Global Warming Potential	TTW	Tank to Wheel
HT-DAC	High temperature direct air capture	vol%	Volume percentage
HTFT	High temperature Fischer-Tropsch	VSA	Vacuum swing adsorption
HTL	Hydrothermal liquification	WGSR	Water-gas shift reaction
HVO	Hydrated Vegetable Oil	wt%	Weight percentage
ILUC	Indirect land use change	WTT	Well to Tank
IQR	Interquartile Range	WTW	Well to Wheel
kWh <sub>el</sub>	Kilowatt hours of electric energy	YSZ	Yttrium-stabilized zirconia
kWh <sub>th</sub>	Kilowatt hours of thermal energy	ZLEV	Zero- and Low-Emission Vehicles
LBM	Liquified Bio Methane		

## 2 SUMMARY

In the upcoming decades, conventional powertrains on-road, maritime and aviation will still play a significant role, even if alternative, zero-tailpipe emission powertrains concepts are gaining momentum and will become predominant. The realization of decarbonization targets requires drastic emission reductions in the transport sector, which most likely can't be achieved by entirely switching to zero-tailpipe emission concepts, since the current fleet will remain in use until the end of its lifespan.

It should be assumed that the global transportation sector will still to a certain, but not neglectable be powered by combustion engines for at least two decades even though the new development of vehicles with internal combustion engines will end and production eventually runs out. Therefore, alternatives to conventional fossil fuels (CFFs) represent a very attractive solution for midterm emission reduction, especially if they are suitable for already on-road vehicles.

While the emissions arising from fuel combustion are known to a high degree of certainty, the environmental impacts from alternative fuels feedstock provision and production process chains are still in an early stage of evaluation. Therefore, this study aims to provide a comprehensive analysis on the production of alternative fuels.

The objective of this report is to evaluate direct and indirect effects on the environmental impacts related to alternative fuel supply to provide a baseline of comparison with the life cycle assessment of the ECOFuel process.

In this case, we used a meta-analysis of recent life cycle assessment (LCA) studies as method. Due to the absence of clear regulations like PEF or PEFCR for fuels, a methodology for the evaluation of environmental impacts related to fuel production was needed. Comprehensive LCA studies were identified to be the best option to ensure transparent and comparable results. LCA is well-suited to this purpose as it evaluates every aspect of a product's lifecycle, as well as its indirect effects.

The uncertainties associated with this method can partially be eliminated by comparing multiple studies and defining plausible emission ranges for different fuel types.

The literature screening process included reading several 100 abstracts of relevant studies. Following multiple phases of study filtering, 24 studies remained for detailed analysis. The results are presented in three categories, namely Fossil Fuels, Synthetic Fuels, and Bio-based Fuels, with fossil fuels as a baseline of comparison. In addition, gaseous fuels have also been included if they have been covered in relevant studies.

Biomass cultivation is identified to be the GWP-, water depletion-, acidification- and eutrophication-hotspot in bio-based fuel production. Land use change, the change in natural carbon stocks, potentially places bio-based fuels far above traditional fossil fuels from a carbon footprint perspective. Acidification and eutrophication are mainly affected by fertilizer use. Water usage during plant cultivation causes the high amount of water depletion related to bio-based fuel production. Utilizing biogenic wastes as feedstock relieves most of the burdens connected to plant cultivation, but the availability of those "advanced" feedstocks is limited. Figure 2-1 gives an overview of the GWP results for bio-based fuels sorted by fuel types.

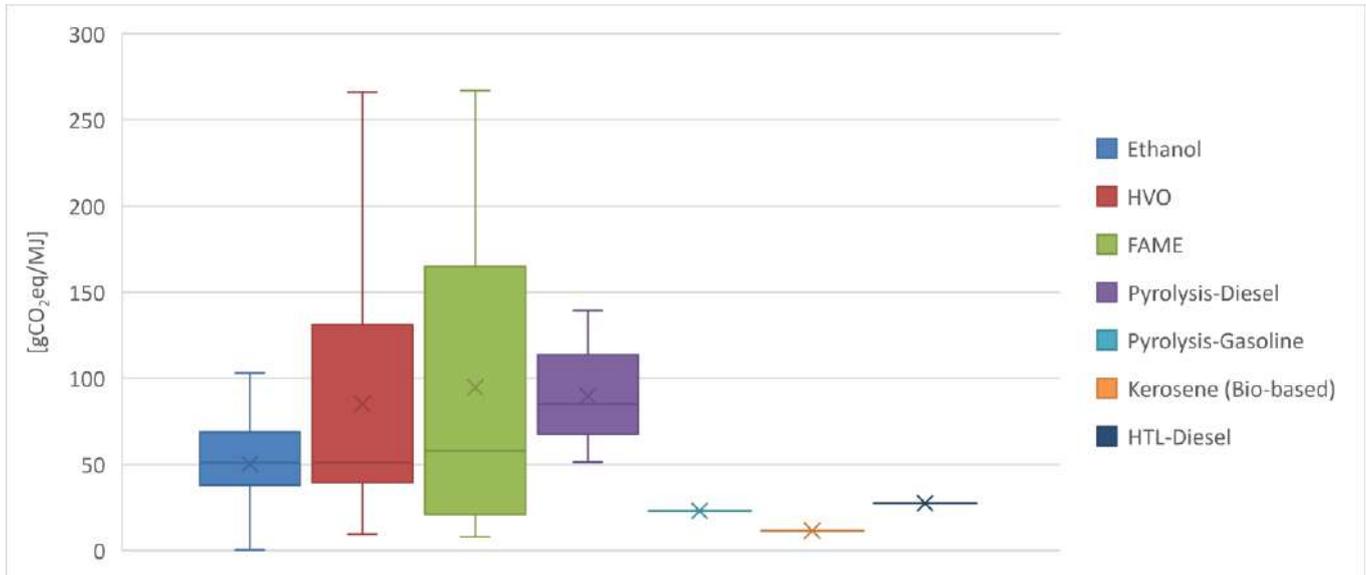


Figure 2-1: Overview on the results of bio-based fuels sorted by fuel type.

Synthetic fuels carbon footprints depend greatly on the carbon intensity of electricity for CO<sub>2</sub> and H<sub>2</sub> provision, as their production comes with a high energy demand. Due to the strong reliance on electric energy the sensitivity towards extreme high as well as low carbon footprints is unprecedented for this fuel class. Impacts from large scale renewable energy provision, especially from photovoltaic construction and decommission as well as from concentrated solar power heat accumulator production are identified to be the main influencing factors for acidification and eutrophication related to synthetic fuel production. The results for synthetic fuels vary widely and show great dependency on the feedstock used. Figure 2-2 and Figure 2-3 show the GWP results for SynBio- and SynNoBio Fuels sorted by the synthetic process used for fuel production.

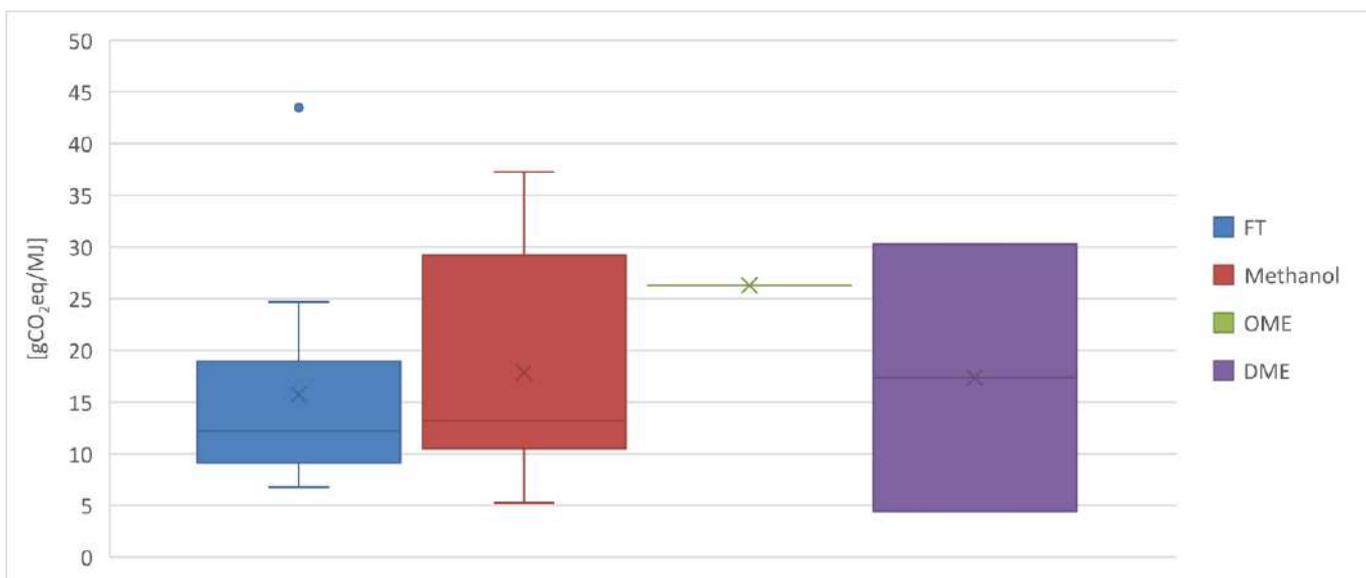


Figure 2-2: Overview on the results of SynBio fuels sorted by synthesis type.

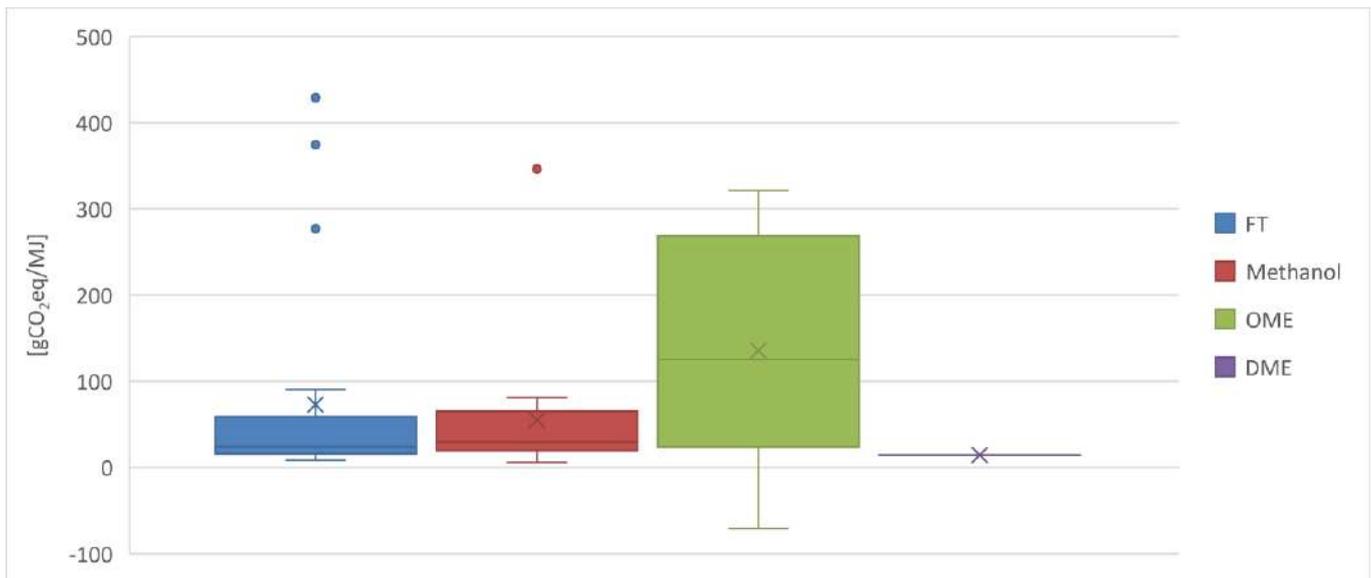


Figure 2-3: Overview on the results of SynNoBio fuels sorted by synthesis type.

Gaseous fuels are evaluated separately but the conclusions concerning their feedstocks remains the same as for fossil, synthetic and bio-based fuels. Gas leakages have a significant impact on the carbon footprint of gaseous fuels, mainly during their transport and distribution.

As alternative fuels from renewable feedstocks rely on carbon that's bound in the short- to midterm before fuel production, their combustion emissions are more or less offset by the carbon binding during feedstock production. This qualifies them as a mean for midterm emission reduction even though environmental impacts from production may in some cases surpass those from traditional fossil fuel production. The extent to which those production related "carbon credits" are considered in LCAs varies, impacting comparability between studies.

In best case scenarios, synthetic as well as bio-based fuels replacing traditional gasoline and diesel offer huge potential for emission reduction in already operational transport vehicles. As the availability of low-carbon bio-based fuels is much more limited, synthetic energy carriers will play a major role in the decarbonization of the transport sector. Low-carbon synthetic fuels require a major expansion in the provision of renewable energy, as the availability of green energy will be the bottleneck for their scale up. The meaning of alternative fuels will depend heavily on future developments. Not only on improvements in process efficiency but mainly in decarbonization of the energy mix and the supply of advanced feedstocks.



### 3 TARGET AND SCOPE OF THE STUDY

One of the overall goals of the EcoFuel project is to perform an LCA of the novel process chain being developed in this project to demonstrate its sustainable and truly green nature, while minimizing or even eliminating the use of rare and toxic materials. To determine a reliable, transparent and objective baseline for this LCA a comprehensive literature review on LCA studies was conducted, comprising a wide range of alternative and fossil fuels, to find representative values of most important environmental impact categories. The findings of this extensive literature review and an evaluation, both from empirical and methodological perspectives, are provided in this report.

The shift from fossil fuels with well-known production pathways to alternative fuels might lead to a variety and even adverse changes in different environmental indicators. Therefore, this study discusses, apart from the global warming potential, the effects on commonly used environmental impact indicators (like toxicity, acidification, eutrophication).

Compared to the mature and established production pathways for fossil fuel, the pathways for alternative fuels are relatively new and still under development, and in some cases not yet realized in large scale industrial applications. To consider these boundaries, as also to provide the intended baseline for the evaluation of the EcoFuel process chain, this study considers the technological readiness levels (TRL) of the respective production pathways and examines projections to 2030 and 2050. Alternative fuel production strongly depends on renewable energy sources, which are as of today not yet available to a sufficient extent. With an increased share of renewable energy in the national energy mixes in the upcoming years, the climate change related burdens of alternative fuels, especially synthetic fuels, will change to the better significantly in the future.

The scope of this study includes fuels for applications in the transport sector, including private mobility as well as commercial transport. This includes road transport, maritime and aviation with a focus on drop-in synthetic fuels.

Specifically, the study aims to answer following questions:

- Are the existing LCA studies for various state-of-the-art fuel pathways for major fuel categories (fossil, synthetic, bio) comparable?
- Is there a common understanding among the considered LCA studies regarding scope, system boundaries, functional unit, multifunctional process handling and data quality?
- Are the results of the studies regarding mid-point indicators with focus on GWP comparable? I.e. can the existing, recent studies provide a robust evidence base for a later comparison with the EcoFuel process chain being developed?
- Is sufficient, robust information existing to be able to detail existing pathways for synthetic fuels and name typical values for important impact categories, taking into account the TRL, in order to later evaluate the EcoFuel process chain?
- Are fuel pathways with different TRL's comparable to each other and how does the TRL influence the GWP?

To answer these questions, an extensive literature study delivered over 100 LCA studies on fuels as input to this study, which met the defined selection criteria as well as the ISO standards and guidelines for conducting LCA studies. After a detailed review of these studies, regarding analysis and detailing of production pathways, system boundaries and allocation methods as well as harmonizing the results for a uniformly functional unit and system boundaries (WTT), 24 studies with 355 data points remained for an analysis and evaluation.

The applied methodology is described in chapter 5. The methodology of the examined studies had to be transparent and fully documented. To evaluate production and resource provision related impacts as good as possible, the chosen system boundary is Well-to-Tank (WTT). The found and selected LCA studies were only converted as far as necessary and only if reliable sources for conversion factors were at hand. Any conversion of values that implied additional assumptions was refrained from.

The extracted datapoints were classified and analyzed by fuel types. Top and low ends of these ranges were examined in depth to explain deviations in LCA methodologies and uncertainties, which are presented in chapter 7.

In future the market success of alternative fuels substituting fossil fuels will not depend on environmental advantages alone but will at the same time depend on the two criteria availability and cost. Therefore, a techno-economic base study was performed in parallel. This analysis, also part of the deliverable D7.1, can be found in part B of this report. The advancement of more sustainable fuels as alternatives to currently used fossil fuels in different transport sectors will be strongly depending on upcoming legislative regulations. Regulations which will have to address both the beneficial use of from an environmental perspective and the investments in new production facilities for more sustainable fuels.

Apart from the above mentioned ecological study on alternative fuels, economic and legislative considerations were carried out.

The results of an analysis of the European legislative regulations currently in place respectively already adopted in these two directions, with respect to their consideration of effects on environmental and economic impact is included in the legislative regulations chapter in the first part of this report. The techno economic analysis on alternative fuels with focus on synthetic fuels is subsequent to this report as part B.

- This study is not an LCA of any dedicated fuel pathway but is intended to serve as a baseline to be able to compare advantages, disadvantages of different production pathways and provide mean values.
- This study is not comparing different methodological approaches regarding their applicability or is not proposing one certain methodology for performance of an LCA on fuel production pathways.

## 4 LCA METHODOLOGY

This study is conducted as a meta-analysis of studies that utilize LCA methodology to evaluate environmental impacts of fuel production pathways (FPPWs). Even though LCA is an established method for environmental assessments, it still yields significant variety in its execution, which can often lead to uncertainties when interpreting results. Most methods have their own legitimization and can pinpoint certain aspects of a system. Taking this into account, the comparison of LCA results across many studies is a compromise of data comparability and data quantity, since few studies apply exactly the same methods. Apart from methodological choices, systematical choices also impact comparability.

LCA is defined and standardized in ISO14040 and ISO14044 as a tool for environmental impact assessment as a “compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle”. As defined in ISO 14040/14044 it consists of four stages [1]:

- **Goal and Scope Definition**

The goal of an LCA states:

the intended application, the reasons for carrying out the study, the intended audience - i.e., to whom the results of the study are intended to be communicated, and whether the results are intended to be used in comparative assertions intended to be disclosed to the public.

The scope includes the following items:

the product system to be studied, the functions of the product system or - in the case of comparative studies - the systems, the functional unit, the system boundary, allocation procedures, impact categories selected and methodology of impact assessment, and subsequent interpretation to be used, data requirements, assumptions, limitations, initial data quality requirements, type of critical review, if any, type and format of the report required for the study.

- **Life Cycle Inventory Analysis**

phase of the LCA involving the compilation and quantification of inputs and outputs for a product throughout its life cycle.

- **Life Cycle Impact Assessment**

phase of the LCA aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts for a product system throughout the life cycle of the product.

- **Life Cycle Interpretation**

phase of the LCA in which the findings of either the inventory analysis or the impact assessment, or both, are evaluated in relation to the defined goal and scope in order to reach conclusions and recommendations.

Further on, the norms allow for modifications to the scope of the study while the LCA is conducted due to the iterative nature of LCA. The items mentioned in the scope definition will be elaborated in the following chapter.

## 4.1 Attributional vs Consequential LCA

Attributional (ALCA) and consequential (CLCA) are the two approaches to conduct an LCA. While ALCA is reliant on average data and is used for attributing known impacts from activities to products, CLCA uses marginal data to evaluate the implications of a change in activity. CLCAs are better suited for decision makers since they assess changes in demand and production as opposed to ALCA which assess current average data. [2] This report includes studies using both approaches to provide the most wholistic overview possible.

## 4.2 Functional Unit

The choice of the functional unit determines what exactly the analyzed product and its unit are. Any impact results are expressed in their corresponding units per functional unit. In fuel related studies the most common functional unit is MJ of produced fuel. In this context, functional units that imply additional assumptions (such as vehicle kilometers, person kilometers, liters, etc.) may be useful in certain scenarios but can yield additional uncertainty. The chosen functional unit for this study is MJ of produced fuel.

## 4.3 System Boundaries

The system boundaries of an LCA study determine the system components which are part of the analysis, and which are not. System components can be processes or flows. All flows that leave the system boundaries are cut off. Typically, criteria for cut-offs are defined to specify which flows are of negligible impact to the system and therefore excluded. Cut-off criteria can be for instance a threshold of a certain metric, below which a flow is excluded from the life cycle inventory calculation. System boundaries must be chosen such that all flows leaving them fulfill the cut-off criteria.

LCA often uses a modal approach, dividing the system into life cycle stages. Those are usually:

- **Cradle to gate**  
This phase includes outputs related to production. Resource extraction, energy production, production facility construction, provision of production equipment and machinery as well as their maintenance and operation, distribution and transport are all activities whose impacts may be presented in a Ctg context – depending on the systematic choices of the LCA practitioner. In the case of LCAs examining FPPWs, Ctg is referred to as Well-To-Tank (WTT).
- **gate to gate**  
Often referred to as use-phase, this phase includes outputs from the use of the product itself. In a fuel context, this would be the combustion of the product. Depending on systematic choices, distribution of the finished product may also be included in this phase. In the case of LCAs examining FPPWs, gtg or the use-phase is referred to as Tank-To-Wheel (TTW).
- **gate to Grave**  
In this phase, the end of the products life cycle is examined. Therefore, it is often referred to as End-of-Life (EoL). Included activities are waste disposal, recycling, or reuse. The EoL phase also counts toward the TTW phase.
- **Cradle to Grave**  
In fuel related studies the whole life cycle is usually referred to as well to wheel (WTW). The schematics of an exemplary WTW system are shown in Figure 4-1. In the case of LCAs examining FPPWs gtg is referred to as Well-To-Wheel (WTW).

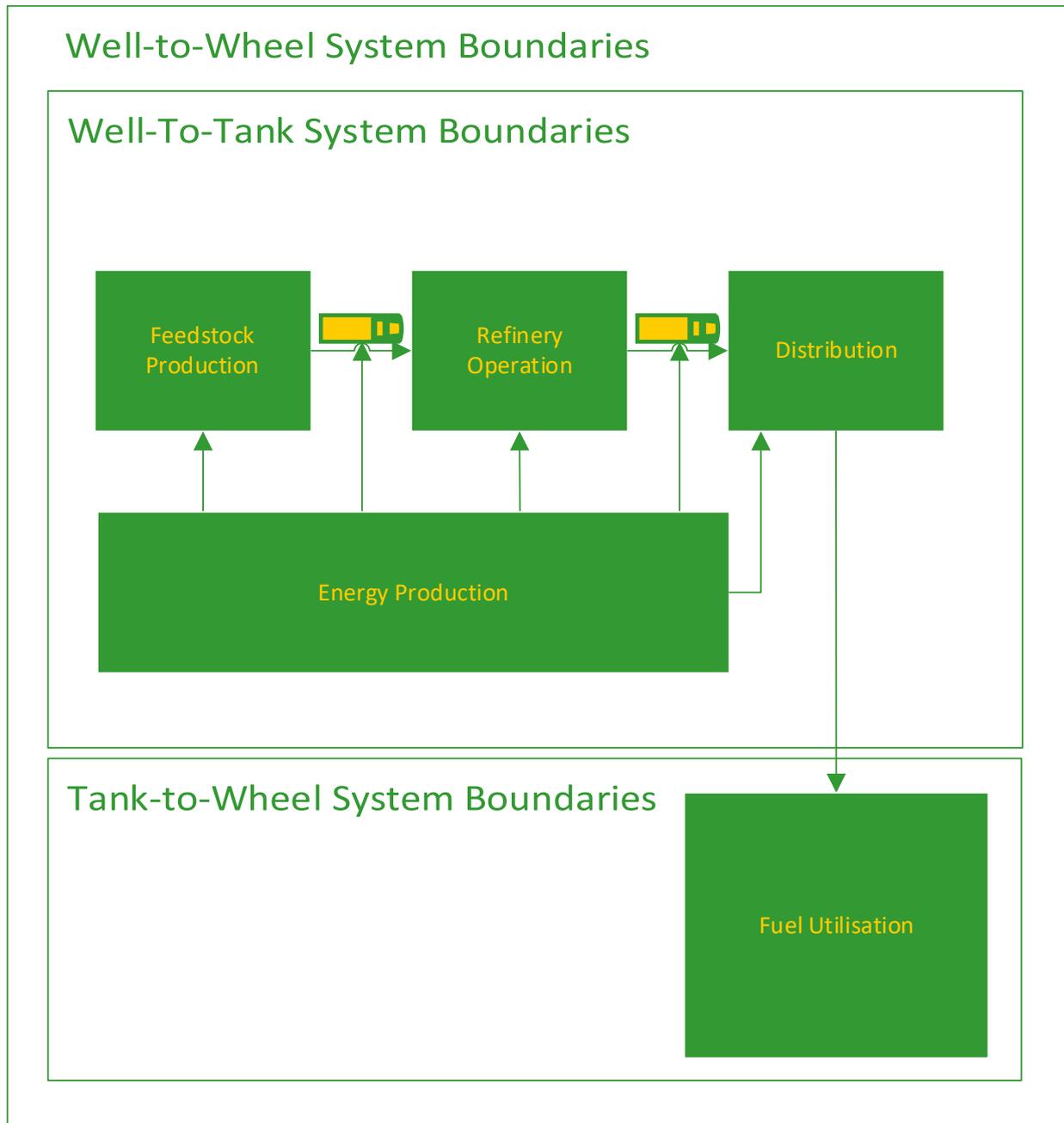


Figure 4-1 : Schematics of a WTW system and its life cycle stages

Since this study examines fuel production, the chosen system boundary is WTT. It should be mentioned that WTT analysis has a much higher degree of uncertainty than tank to wheel (TTW) analysis. This is due to the high number of estimates and assumptions needed for a WTT analysis opposed to combustion in a TTW scenario. In addition, the attribution of impacts to different life cycle phases alters WTT results, while a WTW analysis is indifferent to those choices

#### 4.4 Credits and Carbon Recycling

The carbon crediting approach is one of the most impactful choices when it comes to GWP results. If carbon from a non-fossil source is used as feedstock (i. e. carbon capture and utilization or biomass feedstocks), it is often allocated as a carbon credit (the credit amount is subtracted from GWP results).

For this reason, crediting is most relevant to bio-based and synthetic fuel pathways. Crediting can also occur from negative land use change (LUC) emissions or as substitution credits.

The exact amount of crediting depends on the system boundaries, sometimes leading to credits that even surpass emissions from combustion [3]. The wide variance of decisions when it comes to crediting leads to high variance in results which is shown in the results and discussing section.

### 4.5 Multi-functionality of Production Processes

A production process is multi-functional if it delivers more than one product. An example for this is shown in **Fehler! Verweisquelle konnte nicht gefunden werden..** When performing an LCA on a multiproduct system, the choice on how to attribute the environmental impacts to the products can have severe impacts on the results. Some outputs to the environment can often only be evaluated on an aggregate

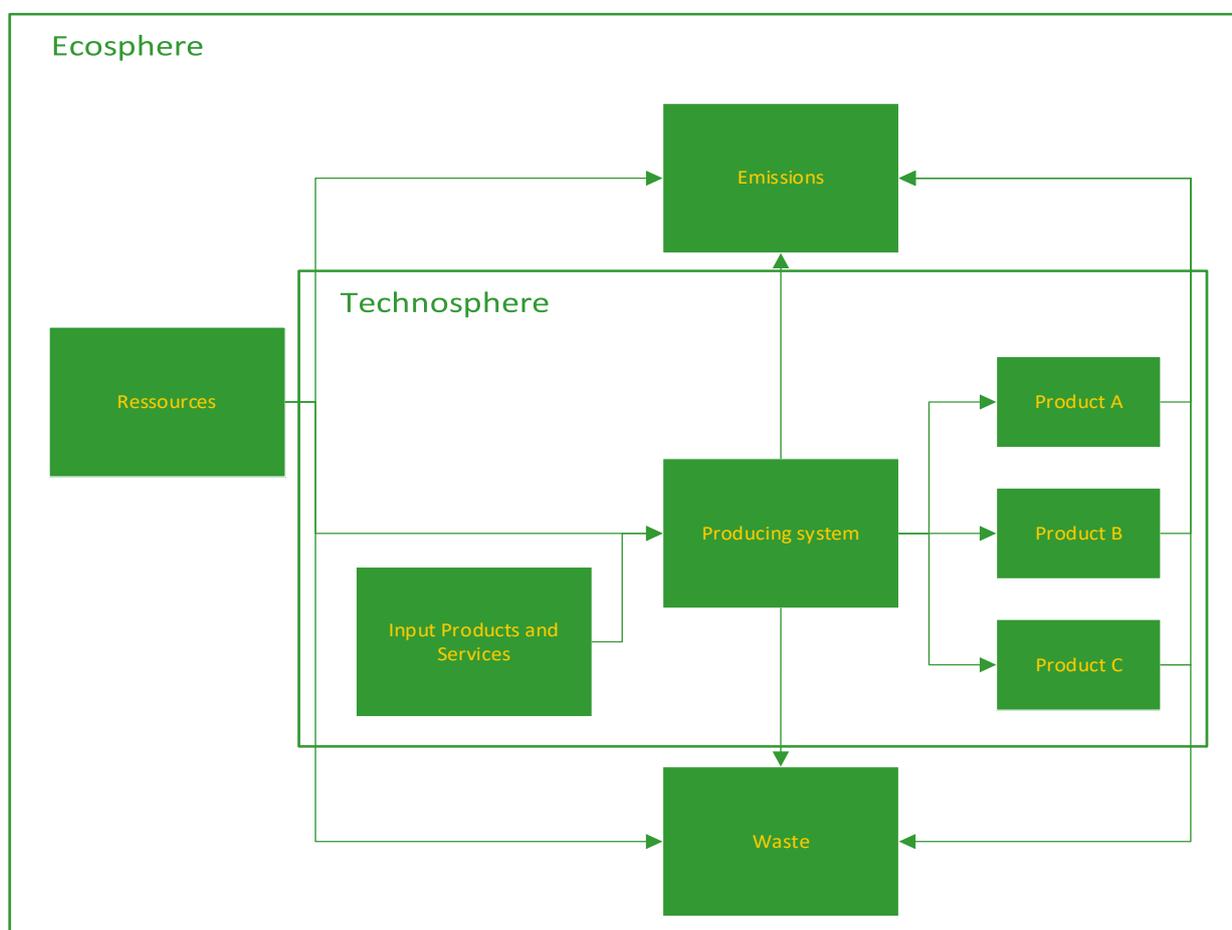


Figure 4-3: Example of a multifunctional producing system

level and have to be partitioned accordingly.

Impacts arising from product utilization or recycling can often be directly evaluated while most flows from upstream activities are only available as aggregates. In some cases, high granularity of primary data can help isolate flows within the system and make attribution more feasible. There are several approaches to solve multifunctionality. Each approach is briefly explained below:

- Allocation compares any common metric of the products and attributes the outputs to the environment according to the corresponding shares of those. Common metrics include weight, energy density, volume, or economic value. The choice of this metric can be very impactful, for

instance, compare the output shares of a multiproduct system producing hydrogen and gasoline, attributed by either mass or volume. Another way of allocation is causal allocation. This method attributes impacts of specific system components to the products they are used for, in contrast to the other allocation methods that treat the producing system as a black box. When analyzing fuel pathways, the most logical allocation metric is energy density.

- Subdivision refers to the process of disaggregating the inputs of a producing system and correlating them to their corresponding outputs. In essence this means to isolate input to output flows inside the system.
- System expansion includes the additional products in the functional unit and widens the system boundaries to include the additional activities.
- Substitution uses comparable product pathways from other studies or models to eliminate unwanted side products via subtraction until only the desired product is left. This requires knowledge of the substituted system component. If projections are in the scope of considerations, it should be noted that the substituted components also change over time. Substitution is the subtractive form of system expansion (which is additive).

The ILCD handbook offers a hierarchy on which solution to choose depending on applicability.

## 4.6 Impact Indicators

Impact indicators are representative values that indicate a systems effect on the environment. Typically, LCA results present values for midpoint indicators.

Midpoint indicators represent the causal link between outputs and their effect on the environment. Effects on the environment themselves are usually referred to as endpoint indicators.

Midpoint indicator results are presented as aggregated values, where different outputs to the environment get characterized based on their assumed impacts. This aggregation of different outputs is carried out using a variety of characterization factors. The ISO standards do not clarify which impact categories or characterization factors should be used, they do state however that their sources have to be clarified in any LCA study. Most studies rely on premade collections of mid- and endpoint indicators and their corresponding characterization factors from literature or software tools. The values of those characterization factors differ and, depending on the composition of the analyzed emissions, can have significant impact on the results. To highlight those differences, some characterization factors for GWP100 are shown in Table 4-1.

Table 4-1: selection of GWP100 characterization factors; GWP100 characterization factors from [4]; [5]; [6]; The Kyoto protocol used the characterization factors from the IPCCs Second Assessment Report. Values in tCO<sub>2</sub>eq/t.

	IPCC AR4	IPCC AR5	Kyoto-Protocol	ReCiPe2016v1.1
<b>Methane</b>	25	28	21	34
<b>Fossil Methane</b>	-	-	-	36
<b>Nitrous Oxide</b>	298	265	310	298

The IPCC reevaluates their characterization factors regularly due to new findings concerning radiative forcing and atmospheric lifetime of GHGs.

In addition, there is a tendency for studies to only evaluate CH<sub>4</sub>, N<sub>2</sub>O and CO<sub>2</sub> since they are the quantitatively most relevant GHGs. This could in some cases lead to an underestimation of GWP results.

Characterization factors often use different units for their indicator results, affecting comparability between studies. A collection of indicators that were observed in the literature review for this study is shown in Table 4-2.

Table 4-2: Overview of midpoint indicators, compiled from the information collected from [7] and [8].

Impact category	Definition	Impact indicator	Damage category	Unit
<b>Acidification</b>	Reduction of the pH due to the acidification effects of anthropogenic emissions	Increase in the acidity in water and soil systems	Damage to the quality of ecosystems and decrease in biodiversity	kg SO <sub>2</sub> equivalent mol H <sup>+</sup> equivalent
<b>Climate change / Global Warming Potential</b>	Alteration of global temperature caused by greenhouse gases	Disturbances in global temperature and climatic phenomenon	Biodiversity decreases in general, Temperature disturbances Climatic phenomenon abnormality	kg CO <sub>2</sub> equivalent
<b>Depletion of abiotic resources</b>	Decrease of the availability of non-biological resources (non-and renewable) as a result of their unsustainable use	Decrease of resources	Damage to natural resources and possible ecosystem collapse	– kg antimony equivalent – kg of minerals – MJ of fossil fuels –m <sup>3</sup> water consumption
<b>Ecotoxicity</b>	Toxic effects of chemicals on an ecosystem	Biodiversity loss and/or extinction of species	Damage to the ecosystem quality and species extinction	– kg 1,4-DB equivalent – PDF (potentially disappeared fraction of species) – PAF (potentially affected fraction)
<b>Eutrophication</b>	Accumulation of nutrients in aquatic systems	Increase in nitrogen and phosphorus concentrations Formation of biomass (e.g. algae)	Damage to the ecosystem quality	– kg PO <sub>4</sub> <sup>-3</sup> equivalent – kg N equivalent
<b>Human toxicity</b>	Toxic effects of chemicals on humans	Cancer, respiratory diseases, other non-carcinogenic effects and effects to ionizing radiation	Human health	– kg 1,4-DB equivalent – DALY (disability adjusted life years)
<b>Land use</b>	Impact on the land due to agriculture, anthropogenic settlement, and resource extractions	Species loss, soil loss, amount of organic dry matter content, etc.	Natural resource (non and renewable) depletion	– PDF/m <sup>2</sup> – m <sup>2</sup> a
<b>Ozone layer depletion</b>	Diminution of the stratospheric ozone layer due to anthropogenic emissions of ozone-depleting substances	Increase of ultraviolet UV-B radiation and number of cases of skin illnesses	Human health and ecosystem quality	– kg CFC-11 equivalent
<b>Particulate matter</b>	Suspended extremely small particles originated from anthropogenic processes such as combustion, resource extraction, etc.	Increase in different sized particles suspended on air (PM10, PM2.5, PM0.1)	Human health	– kg particulate matter
<b>Photochemical oxidation / Photochemical ozone formation</b>	Type of smog created from the effect of sunlight, heat and NMVOC and NO <sub>x</sub>	Increase in the summer smog	Human health and ecosystem quality	– kg ethylene equivalent (C <sub>2</sub> H <sub>4</sub> ) – kg NMVOC – kg formed ozone
<b>Ionizing Radiation</b>	Release of radionuclides originated from anthropogenic processes such as energy generation (e.g. nuclear).	Damage to human health and ecosystems linked to the emissions of radionuclides.	Human health	kBq U-235

## 4.7 Land Use Change

Another uncertainty in GWP results arises from the valuation of direct- (DLUC) and indirect land use change (ILUC). LUC is especially relevant for biogenic feedstock production. It is expressed in CO<sub>2</sub> equivalents, reflecting the loss of natural carbon binding capacity. DLUC refers to the change in carbon stocks from land that's converted to be used for a specific activity. ILUC refers to carbon stock changes that arise from compensating a change in activity somewhere else. For instance, the use of biomass that would be usable as animal food leads to ILUC, since the foregone food needs to be produced somewhere else. Even though LUC is most relevant in biomass reliant pathways it can impact carbon footprints for all fuel classes. Another problem in comparability arises here, since not all LCA studies evaluate emissions connected to LUC. In addition to this, the evaluation of ILUC yields additional uncertainty since the exact nature of the converted land can in most cases only be assumed. The carbon burden emerging from LUC is very dependent on the nature of the converted land – in certain cases it can even be negative to reflect an increase in carbon uptake (e.g., when converting desert to farmland). The valuation of DLUC comes with less uncertainty since the nature of the converted land can be directly evaluated. From a CO<sub>2</sub> perspective, the worst case for LUC is the conversion of forest land which is way more likely to occur as a consequence of the production of some particular feedstocks than others. The impacts of LUC on LCA results for different fuel classes will be discussed in detail in the results section.

## 5 METHODOLOGY

In this chapter the process of the literature research and review is elaborated. First, the methodology used for the research and review is discussed. The second part summarizes the coverage of the found literature. The analyzation and interpretation of the extracted data is carried out in chapter 7.

### 5.1 Review Methodology

The process for literature collection was inspired by the Rapid Evidence Assessment (REA) methodology according to the guidelines stated in [9]. In compliance with the mentioned guidelines the REA involves the following steps as shown in Figure 5-1:

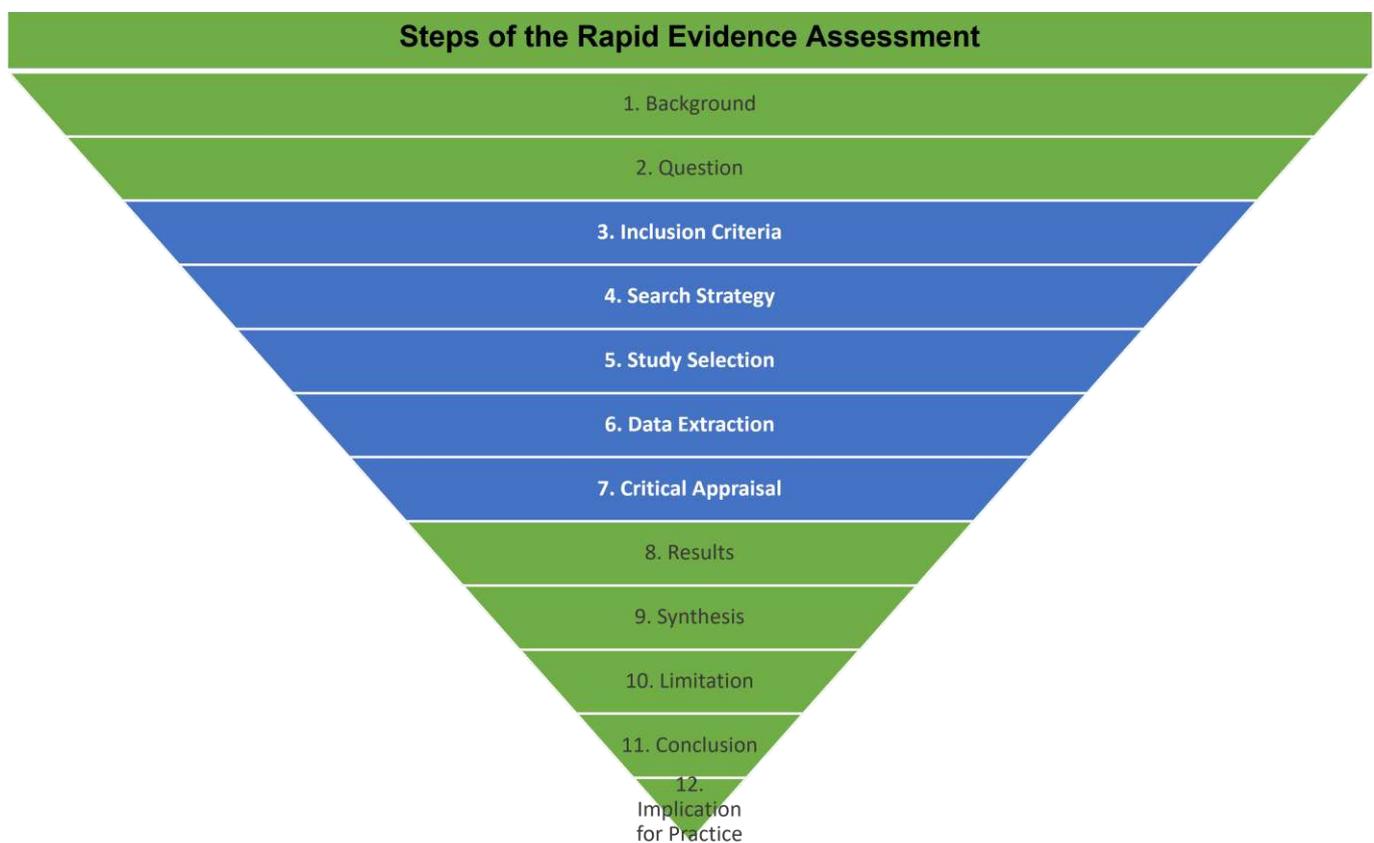


Figure 5-1: Steps in the REA process [9].

#### Inclusion Criteria

The inclusion and exclusion criteria were pre-defined attributes to determine if a study is eligible for the REA or not when reviewing its abstract and later on its full text [9]. Exclusion criteria are red flags, which exclude a study from consideration, even if all inclusion criteria are met. The respective criteria are listed in Table 5-1.

Table 5-1: Inclusion and Exclusion criteria for the literature research.

Inclusion Criteria	
<b>Date</b>	Publications from 2013 to 2021 (End determined by the timeframe of research)
<b>Language</b>	English, German
<b>Type of Studies</b>	Papers, Reports, Articles, Master-Theses and Dissertations
<b>Study Design</b>	Consequential and Attributional LCA
<b>Measurement</b>	LCA studies evaluating the WTT GWP of FPPWs with MJ as FU
<b>Outcome</b>	WTT GWP per MJ of produced fuel
<b>Context</b>	LCA related to FPPW, focusing on alternative FPPWs in the EU
Exclusion Criteria	
<b>Pathway</b>	FPPWs in lab scales (ea. Low TRL)
<b>Fuel</b>	Experimental fuels

### Search Strategy

For the literature collection, LCA publications of recent years have been prioritized. In the literature search, databases such as Google Scholar, Science Direct and Research Gate were used. In addition libraries, publications and studies of renowned institutions and companies were searched.

A reference screening of found studies was also conducted to identify additional available literature. In total more than 100 study titles and abstracts have been screened during the search query.

### Study Selection

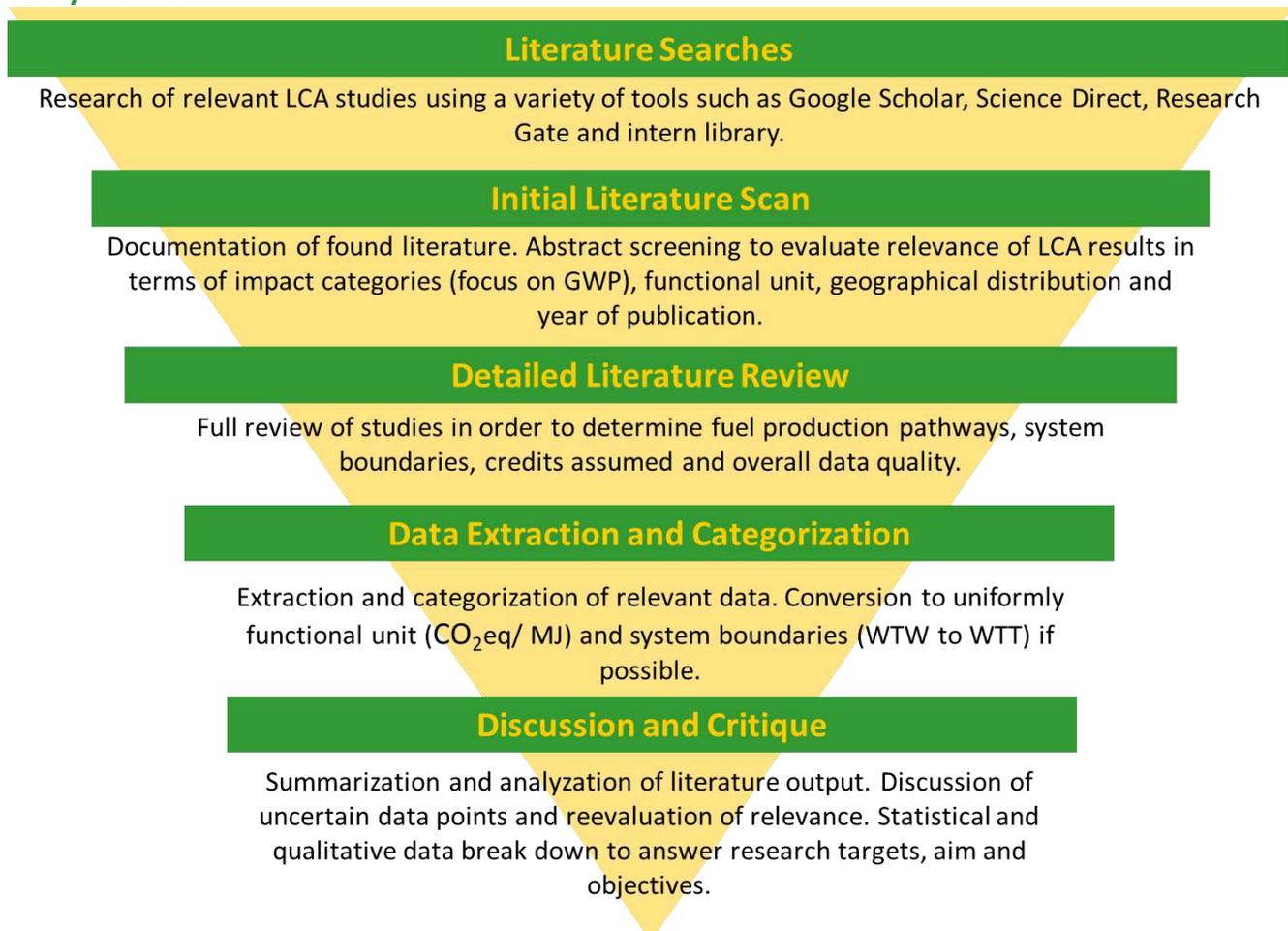


Figure 5-2: Strategy for literature search.

The approach taken for the literature selection is summarized in Figure 5-2. The remaining literature is fully reviewed in the next step. Literature selected for the full review amounted to 72 studies. Available supplementary material was also reviewed to obtain more detailed information on some LCA models. Literature with questionable assumptions like exaggerated CO<sub>2</sub> crediting, unclear system boundaries or production pathways were discarded. After those steps the number of included studies fell to 40. The remaining literature was also scanned for information of secondary relevance, such as economic considerations and data on non GWP midpoint indicators.

### Data Extraction

Subsequently the data points with information of primary and secondary relevance were extracted. The classification criteria for data to be of primary or secondary relevance are shown in Table 5-2.

Table 5-2: Classification of information used in this study.

Information Classification	
Primary relevance	Secondary relevance
WTT GWP in [gCO <sub>2</sub> eq/MJ]	GWP in [gCO <sub>2</sub> eq/MJ] in other life cycle phases
Fuel specification, name and type	Flag: Concern of TRL
Feedstock type, name and type	Flag: Sensitivity analysis
System boundary description	Flag: Economic analysis
Date of publication	Additional Midpoint Indicators
Time frame of data points / projection	
Applied methods	

Information of primary relevance covers the direct interest of this study and the scope of the performed LCA. Information of secondary relevance does not align with the direct interest of this study, nor is it needed to assess either the quality or relevance of the conducted LCA. Often these are only flags, if a certain aspect like TRL has been concerned in a study or not. Secondary information may be useful for future work or in the conversion of GWP from other life cycle phases to the WTT phase.

The GWP in gCO<sub>2</sub>eq/ MJ is the desired functional unit. Some values were converted from other functional units using energy density (for fuels this is the lower heating value - LHV) and density values as stated in the corresponding paper, or if they were not explicitly stated, they were taken from [10]. This study was chosen as a backup for energy density values due to its methodological credibility and coverage of pathways. If conversion was infeasible due to lack of specifications, the corresponding study was discarded.

Furthermore, the WTT GWP is calculated from other life cycle phases (e.g., extracting the TTW outcomes from the WTW GWP results) in some cases. Since WTW system boundaries for fuel related LCA models are common, many TTW and WTW values were observed during the literature screening for this report. A summary of inclusion criteria can be found in chapter 0 Most studies include distribution and transport of the finished product in their WTT system boundaries. The specific WTT system boundaries of the analyzed studies vary and while some of the specifics would amount to negligible differences in the final values (i.e., transport distances, exact cutoff criteria for waste streams etc.), others have greater impacts on the study's results.

If the conversion to the desired functional unit or the extraction of the WTT GWP from different life cycle phases is not feasible in a plausible way, the concerned literatures are excluded. In total, data points for 554 FPPWs from 31 studies have been extracted during the process.



## Data Quality Analysis

During the data quality analysis 203 data points were excluded from analyzation. The remaining data points can be split into two categories. Projected data with a time horizon of 2030 (N=29) or 2050 (N=64) and current data (N=258). Current data covers studies published from 2013-2021 and represent the status up to 2021.

In 19 cases it was not possible to convert the GWP values from a different into the desired functional unit without additional assumptions, which entails the exclusion of those data points. During the result synthesis of this study, further unclarities concerning some data points have arisen. Each of those data points sources got reviewed and discussed thoroughly. During this process, 12 data points were excluded. The rest of the omitted data points was excluded by selecting the most relevant pathways from studies that offer multiple scenarios. In the end, a total amount of 351 GWP values from 24 studies build the database for this studies analysis.

## Critical Appraisal

The remaining included studies are conducted according to or based on well established guidelines like REDII or standards as ISO14040 in general. Deviations from such guidelines or standards are well argued and the accompanying shortcomings acknowledged. The scope and system boundaries of the studies are well defined and the life cycle inventory well documented. Allocations and crediting have been carried out with plausible and comprehensible values.

## 5.2 Literature Coverage

In this section the scope of found literature is discussed. This provides a regional, temporal and fuel coverage overview as well as a coverage of impact categories. As stated before, no results are displayed here.

### Attributional and Consequential LCAs

Most of the analyzed studies are ALCA, with only [10] being consequential. CLCAs are usually more fit for decision making since they assess changes in demand and production. Yet almost all LCA studies that were found in the literature screening are ALCAs, as they still serve as a valuable base of comparison for EcoFuel since the goal of this study is to assess current environmental impacts of fuel production.

### Projections

Projections or projected data points are an estimate of a future FPPW scenarios based on scientific assumptions concerning the development of the utilized energies and technology and therefore provide an outlook for future scenarios. The projected time horizons found in literature are either at the year 2030 or 2050, with 2050 being the favored one. Overall, 26.2% of the data found refer to future scenarios where 18% (N=64) are projected values for 2050 and 8.2% (N=29) for ones in 2030 (see Figure 5-3).

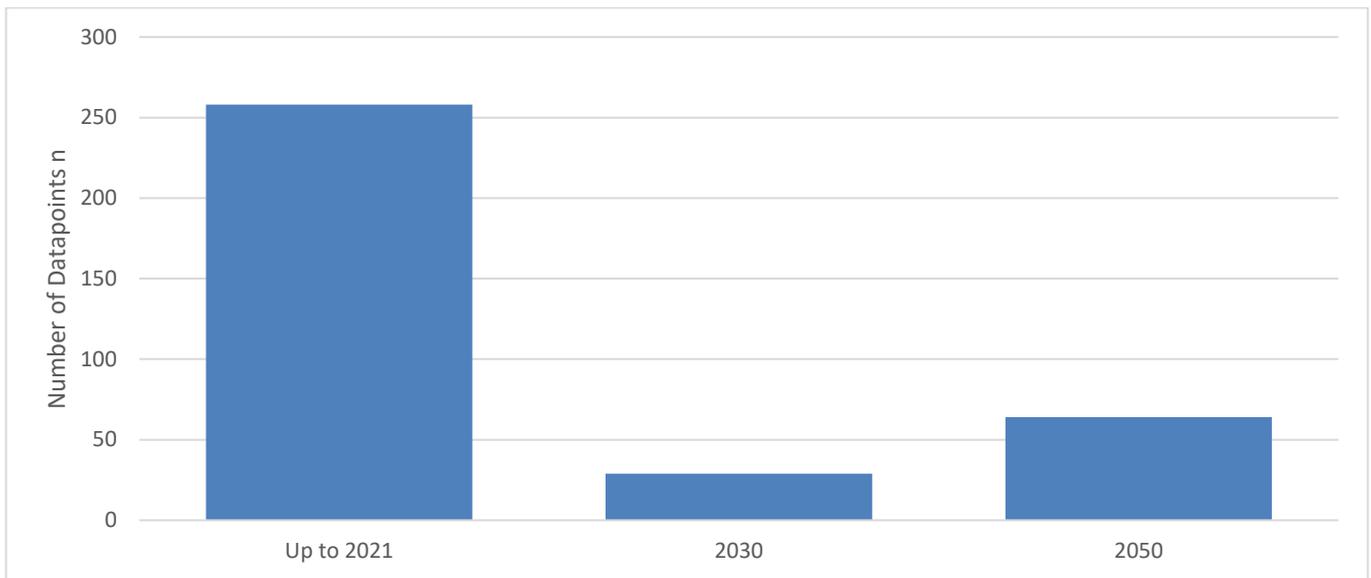


Figure 5-3: Temporal coverage of literature, number of literature N=24. The bars represent the amount of data points which are projected into 2030 or 2050 respectively or are not projected at all.

The time horizons of 2030 and 2050 align with the intermediate and long-term goals for CO<sub>2</sub> emission reduction of major economic regions like the USA and Europe. China has set the same time frame for their intermediate goal, but targets carbon neutrality by 2060.

### Year of Publication

The temporal scope for data collection is defined in the inclusion criteria and reaches from 2013 to 2021. Figure 5-4 shows that the majority of data points lies within the last five years (2021-2017), which is 87% of the data. If only non-projected data points are taken into consideration the percentage reduces to 82%.

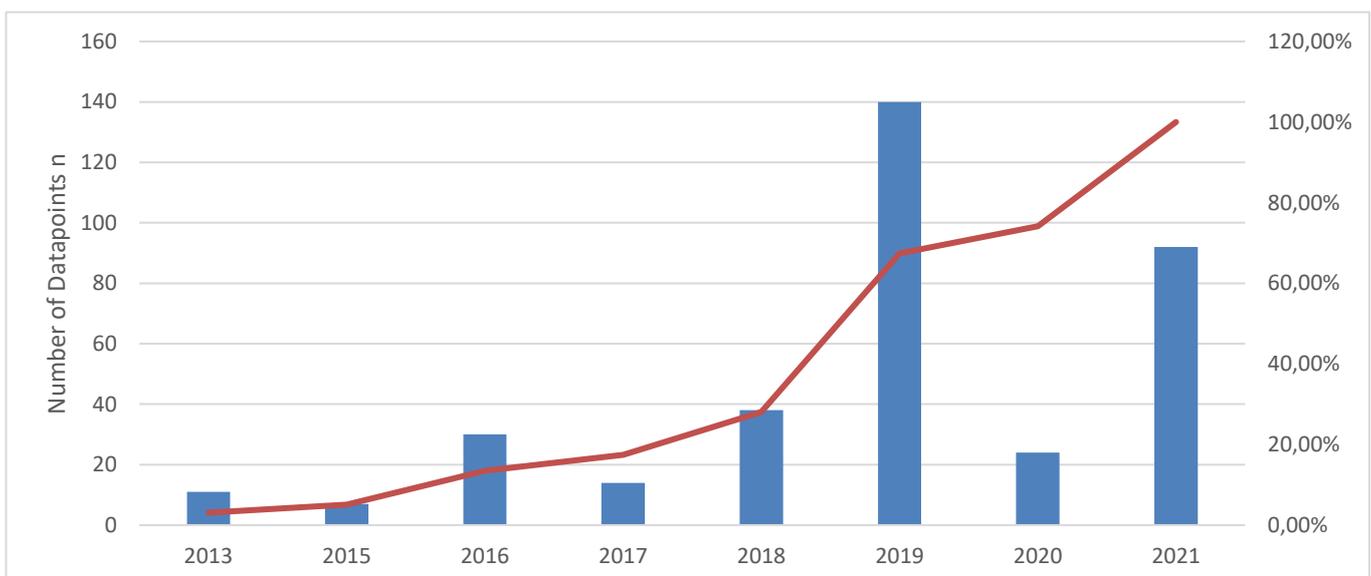


Figure 5-4: Literature by year of publication with projections, number of literature N=24. The bars represent the amount of data points extracted from literature published in a certain year. The line shows the cumulative percentage of data points over the year of publication.

### Regional Coverage

Main focus of this study is the European union. Three quarter of the included studies are providing data for FPPWs in the European Region. In terms of data points this translates to a share of 71.3 % as shown in Figure 5-5. Literature included with the geographical scope outside the European region shows good

methodologic and high-quality scientific work and covered relevant technology pathways. The same holds true for studies where the geographical scope is not specified.

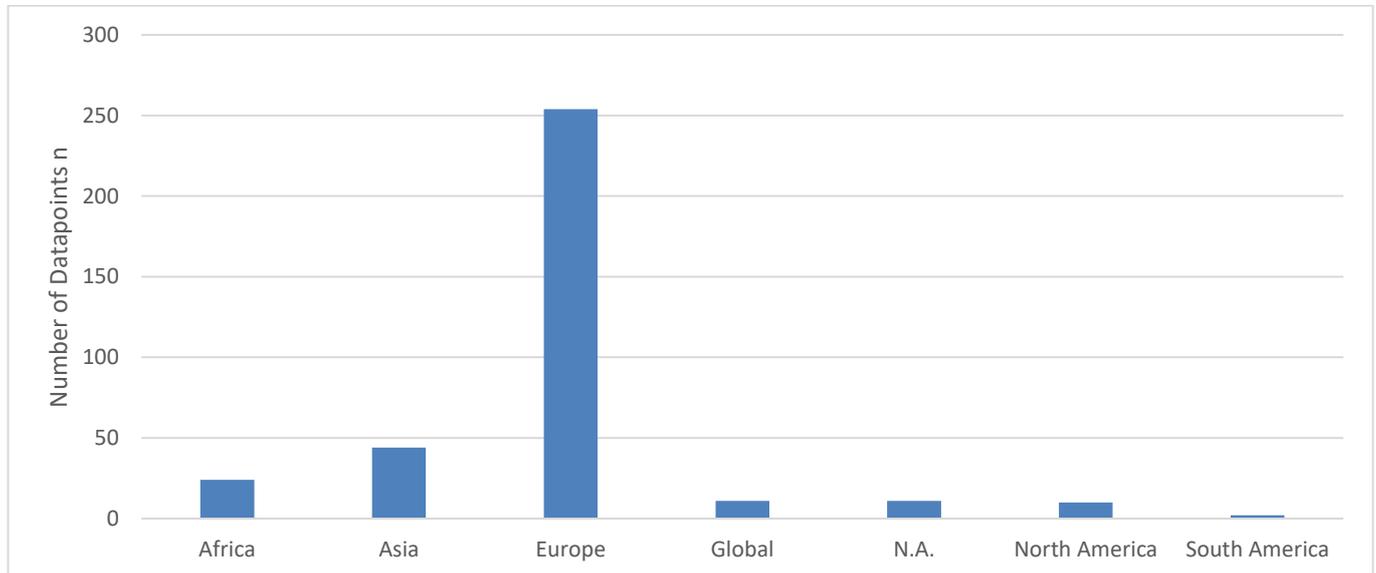


Figure 5-5: Geographic coverage of literature, number of literature N=24. The bars represent the share of data for a certain geographic region on a continental scope.

In Figure 5-6 the geographic scope of the included literature concerning the European Region is depicted. Most studies are focused on the European Region (35.5%) or solely on Germany (47.6%). The great share of literature concentrating on Germany is because they are a major contributor in the European fuel industry as the country with the highest primary refinery capacity and refineries by number [11]. Furthermore, Germany produces biodiesel in large scales and was by 2019 the largest producer of total energy in the EU [12]. Additionally, Germany has the largest gross domestic product in the European Region [13].

The focus on the European Region in the literature can be argued by electricity mix considerations. Due to high trading volumes of electricity within the states of the European region it is plausible to conduct an LCA with the European electricity mix, if the FPPW scenario is placed within the European Region.

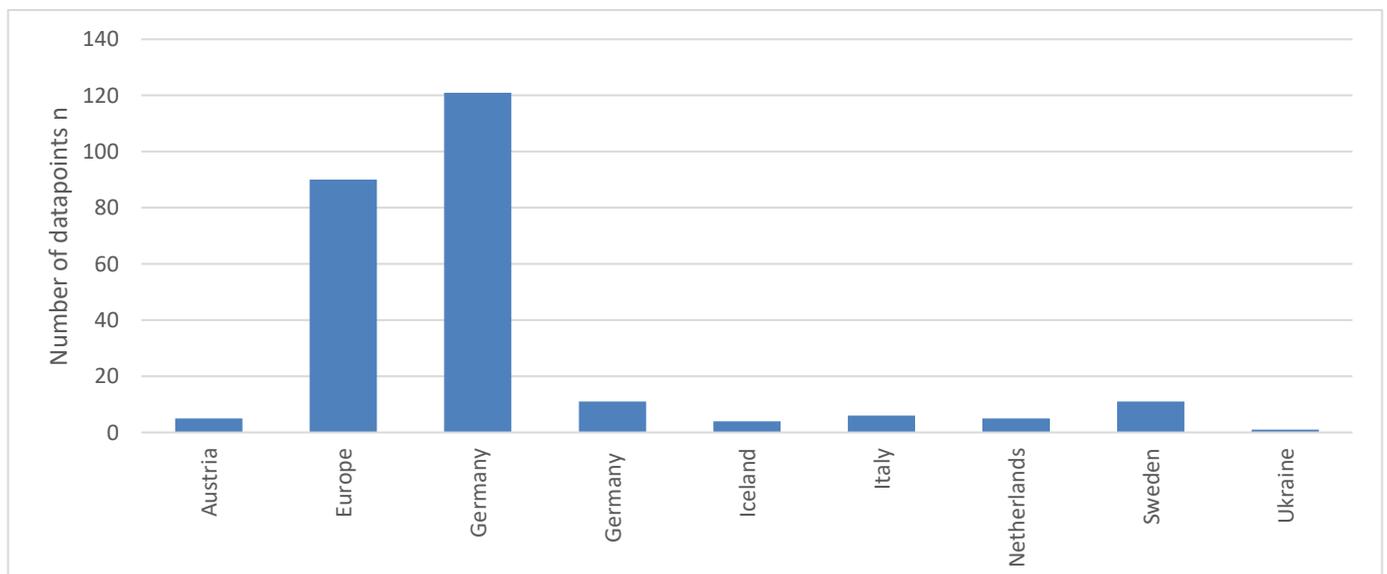


Figure 5-6: Geographic coverage of literature in Europe, number of literature N=24. The bars represent the share of data for a certain part of the European Region.

### Fuel Type Coverage

In chapter 6.3 a fuel type classification is provided and used for this evaluation of fuel type coverage. In Figure 5-7 the shares of the accumulated literature concerning the fuel classifications are depicted. The exact distribution of the extracted data points from the collected literature is presented in Table 5-3.

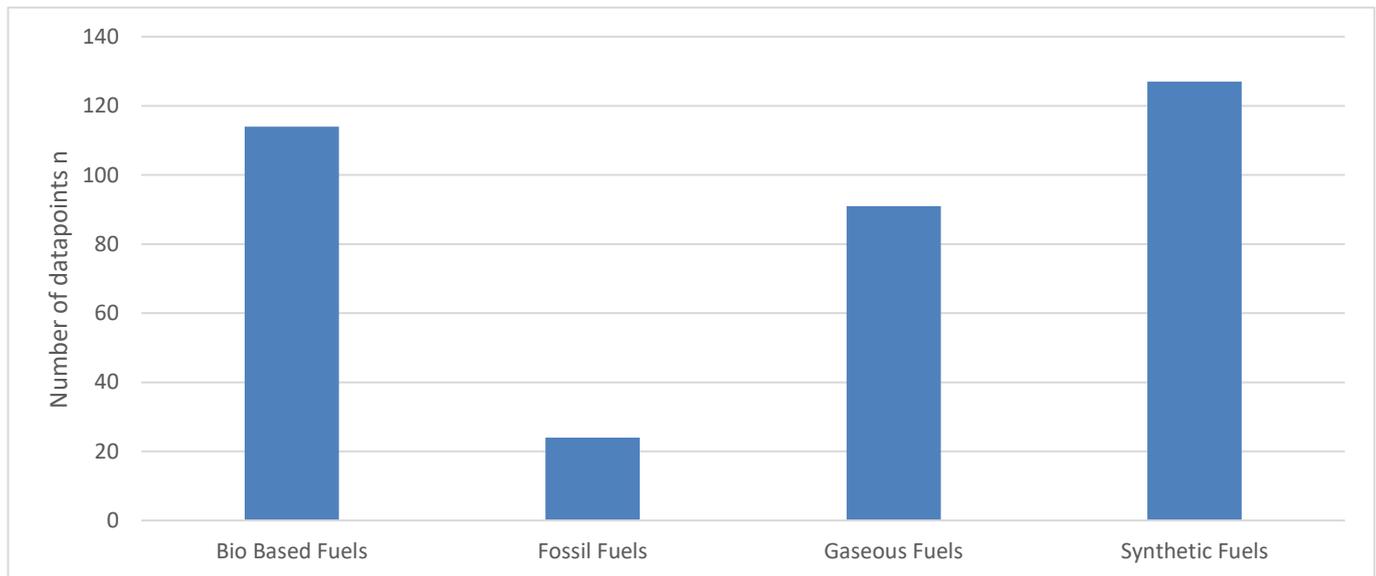


Figure 5-7: Fuel classification coverage, number of literature N=24. The bars are representing the share of data for a certain fuel classification.

Table 5-3: Share of literature for each fuel classification. As one literature might cover more than one fuel classification, the sum of all shares of literature exceeds 100%.

Literature Collected		
Fuel Type	Share of Literature	Share of Data Points
Synthetic Fuels	41.7%	35.7%
Bio-based Fuels	37.5%	32.0%
Gaseous Fuels	58.3%	25.6%
Fossil Fuels	25%	6.7%
<b>Sum</b>	<b>162.4%</b>	<b>100%</b>

The sum of the shares of literature for all fuel types exceeds the total of 100%, because a lot of literature covers more than one fuel type. The share of data points covers all fuel classes by the amount of data collected and will be referred to in the following analyzation. For every fuel class there is one or more sources dominant in terms of extracted data points. Gaseous fuels show the most even distribution of data points over the literature. The effects of dominant literature are discussed in the results and discussion chapter. Following the focus on synthetic fuels this class provides the most data points. The amount of collected data proofs to be sufficient throughout all fuel classes for analyzation and discussion.

### Mid-point Indicator Coverage

As stated in the LCA methodology chapter a LCA not only consist of GWP results but should take additional environmental impact categories into consideration. There are six sources (25%) and 143 data points (40.3%) covering additional environmental impact categories.

In Figure 5-8 the shares of literature, which provides values for a respective impact category are depicted.

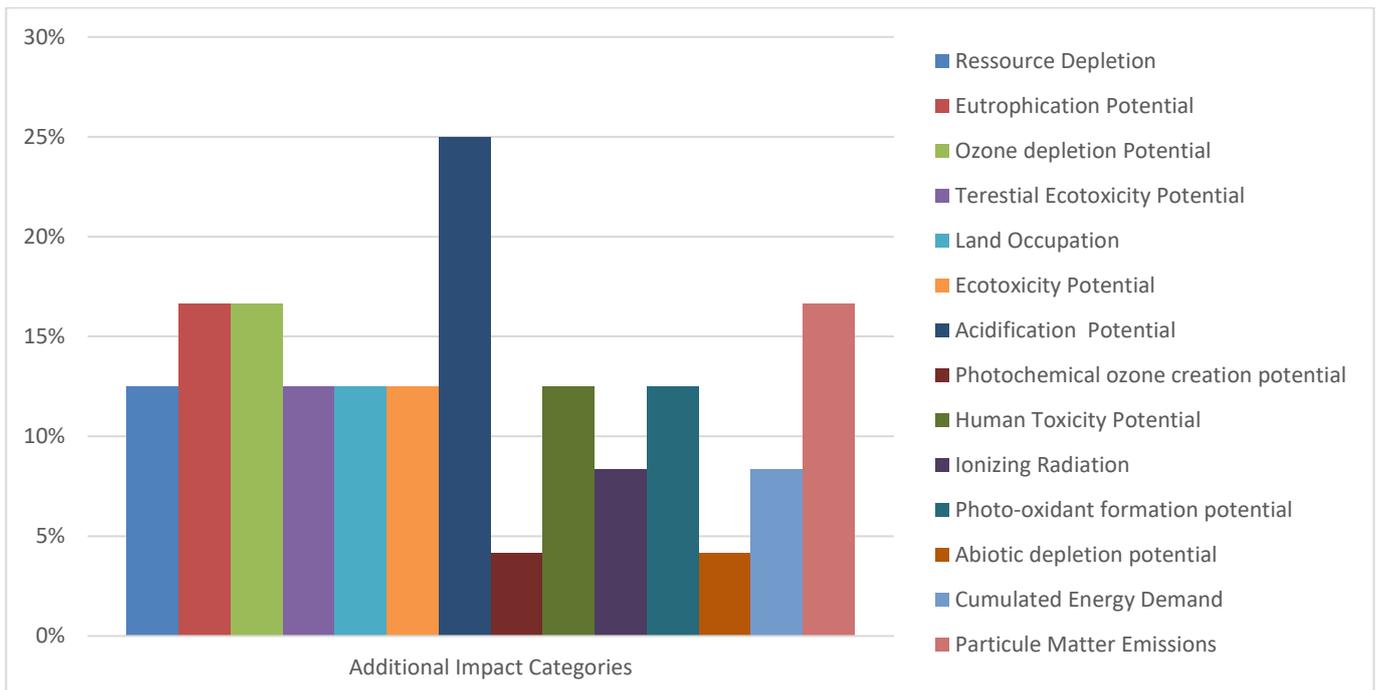


Figure 5-8: Midpoint indicators covered by literature. number of literature N=24. The bars represent the share of literature, that evaluates the respective indicators.

The impact category Acidification Potential is represented the most, especially in hydrogen production as an intermediate process according to [14]. The categories Photochemical Ozone Creation Potential and Particulate Matter Emissions are represented by the least amount of literature. The remaining impact categories are mostly represented by a 13 % share of literature, with a maximum of 17 % and a minimum of 4 %. Striking is the discrepancy between the share of literature containing values for additional impact categories (25 %) and the number of values for additional impact categories for FPPW (40.3 %) available.

## 6 FUEL – STATE OF THE ART

This section includes the analysis of production pathways of fuels that can either be used as a drop-in replacement for traditional fuels or blended for subsequent combustion in ICEs or gas turbines. Fuels for utilization in fuel cells are not considered. Drop-in fuels are fuels which can fully substitute their fossil counterpart. In some literature, so-called “near drop-in” fuels are also counted as drop-in fuels. Near drop-in fuels are fuels which need considerable adjustments to engine and other parts. A list of conventional and alternative fuels and their drop-in capability is shown in Table 6-1.

Table 6-1: Overview of classic fuels and possible substitutes, \* $C_n = C_nH_{2+2n}$ , \*\*  $n = C_{14} - C_{20}$ , \*\*\*  $n \geq 2$ .

Fuel Name	Chemical Composition	Drop-in	Corresponding Norm
Butanol	$C_4H_9OH$	No	-
CNG/LNG	$CH_4$	Yes	DIN51624 (CNG) EN167262 (CNG) EN589 (LNG)
Diesel	$C_{14} - C_{20}$	Yes	EN15940 EN590
DME	$C_2H_6O$	No	ISO 16861
Ethanol	$C_2H_5OH$	No	EN228 (E5/E10) EN15293 (E85)
FAME	$CH_3(CH_2)_nCOOCH_3^{**}$	No	EN590 (B7) EN16734 (B10) EN16709 (B20/B30) EN14214 (FAME)
Gasoline	$C_5 - C_{12}$	Yes	EN228
HVO	$C_5 - C_{22}$	No	EN15940 (Paraffinic Fuels)
Kerosene	$C_{10} - C_{16}$	Yes	-
LPG	$C_1^* - C_4$	Yes	-
Marine Diesel Oil	$C_{20} - C_{70}$	Yes	-
Methanol	$CH_3OH$	No	-
OME	$H_3CO(CH_2O)_nCH_3^{***}$	Yes	-

### 6.1 Fuel Types

This chapter gives a short overview on existing fuels and their possible alternatives or substitutes. The focus of this study is on alternative fuels that directly substitute their fossil counterpart, such as gasoline or diesel replacements, sustainable aviation fuels (SAF) and substitutes for marine diesel oil. Other fuel alternatives such as methanol, dimethyl ether (DME), polyoxymethylene dimethyl ethers (OME) and butanol are also analyzed, but from a more superficial point of view. Table 6-1: Overview of classic fuels and possible substitutes

#### Gasoline

Is a mix of hydrocarbons with carbon-chain lengths from  $C_5$  to  $C_{12}$ . It is typically distilled from crude oil and enhanced with additives. There are several alternatives to fossil derived gasoline. Ethanol, an alcohol with 2 carbon atoms, is already broadly used, and usually blended with fossil derived gasoline. Typically blends of 5 % (E5) or 10 % (E10) ethanol are sold in Europe. The problem of using higher blend percentages of ethanol is its high corrosion and degradation ability of metals, polymers, and elastomers as well as its

low vapor pressure and low energy content. Therefore, minor changes to the engine and fuel system are necessary, especially the substitution of materials that are directly exposed to the fuel. Other applications of Ethanol are the use of E85 in flexible fuel vehicles or usage of E100 in dedicated vehicles. Most part of ethanol production is derived from biomass. It can be obtained by fermentation of sugar or starch biomass. Alternatively hydrolyzed lignocellulosic biomass can be used as source for the fermentation process. Only a small amount of ethanol is produced via synthetic pathways. Another biomass derived alternative is bio crude oil from DTL of lignocellulosic biomass. The produced oil can be distilled in a similar manner to crude oil. Synthetic gasoline can be produced via several pathways which are discussed in the according sections.

### Kerosene

Kerosene or paraffins are a mix of hydrocarbons with carbon-chain lengths  $C_{10}$  to  $C_{16}$ . Fossil kerosene is distilled from crude oil. The term SAF for alternative jet fuels is widely adopted in literature. There are several bio-based and synthetic alternatives to conventional fossil kerosene, which will be discussed in the according sections of this study. Current aircrafts can use SAFs in a blending ratio of up to 50 % with conventional kerosene without the need of modifications and within compliance of current regulations. Higher blending percentages may require engine and fuel system modifications. According to IATA, less than 1 % of the kerosene uplift worldwide are SAF [15].

### Diesel

Diesel is a mix of hydrocarbons with carbon-chain lengths from  $C_{14}$  to  $C_{20}$ . Fossil diesel is distilled from crude oil and further upgraded to improve its properties. To distinguish fossil derived diesel from its alternative variations, the term petro-diesel is established in literature.

Bio derived diesels include a high variety of production pathways and high research effort is expended. Typically, oil from biomass is used in a transesterification process to produce fatty acid methyl ester (FAME), or hydrotreated to yield hydrated vegetable oil (HVO). These diesel substitutes are generally blended with petro-diesel to decrease the carbon footprint of mineral diesel. Whereas FAME is not suitable as a drop-in replacement as it is a solvent and attacks the sealing system of the engine, HVOs theoretically are. A drawback of HVOs is a lower density than the allowed range given in the EN 590 for diesel fuels and therefor needs further treatments to meet the requirements. Additionally, biomass derived diesel can be produced via DTL processes.

Synthetic diesel can be obtained via several pathways. Similar to syn-gasoline, syn-diesel is almost exclusively produced via catalytic synthesis of syngas.

### Marine Diesel Oil

Marine diesel oil is a blend of heavy fuel oil and crude oil distillates. Both fractions are hydrocarbons with long carbon chain lengths of  $C_{20+}$ . Where distillates, also known as marine gasoil, consist only of components from crude oil which evaporate during the fractional distillation process, heavy fuel oil is the residual of this process.

There are several bio-based and synthetic alternatives to conventional fossil marine diesel oil, which will be discussed in the according sections of this study.

### Methane and LPG

Methane is a gaseous fuel and comes in different variations of use. Fossil derived methane, which is cleaned natural gas, is used in compressed and liquified form. Alternatives do exist in form of biomass derived methane and synthetic methane. Biomass derived methane is mainly produced from digestion of wet waste biomass. Subsequently the biogas has to be upgraded into methane. Synthetic methane can



be derived from various feedstocks which are suitable for syngas production. Methanation of the syngas leads to synthetic methane as well.

Since the product of both alternatives is methane as in its fossil derived parent, the already existing infrastructure for transport and distribution can be used with no adoption necessary.

The second gaseous fuel is liquified petroleum gas (LPG) or Autogas. It is mainly a mixture of propane and butane which are derived from distillation of crude oil with chain length of 1 to 4.

### **Methanol**

Methanol is an alcohol with one carbon atom. It can be used for blending with gasoline within the limitations in the fuel specification, used in Flexible Fuel Vehicles as M85 or directly utilized in dedicated M100 vehicles. The problematics of using higher blends of Methanol lay within its high corrosion and degradation ability of metals, polymers, and elastomers as well as its low vapor pressure and low energy content. Therefore, minor changes to the engine and fuel system are necessary, especially the substitution of materials in direct contact with the fuel. Production of methanol is mostly done by catalytic synthesis of syngas. Currently under research is the direct fermentation of methane to methanol.

### **DME**

Dimethyl ether is the simplest ether consisting of an oxygen atom and 2 methyl groups. It is aggressive against polymers and elastomers as well as to some metals. Its lubrication qualities are very poor, and it is gaseous under ambient conditions. Compared to Diesel its energy content is about half the amount. DME cannot be used in Flexible Fuel Vehicles and even small blends of DME in diesel need minor adoptions in the car because of the above-mentioned reasons. DME synthesis has methanol as starting point which is transformed via a catalytic synthesis to DME.

### **OME**

Polyoxymethylene dimethyl ethers are oxygen containing oligomers, with the oligomer being methyl ethers. Short length OME<sub>3-5</sub> can be used for blending with diesel or as drop-in replacement. The combustion of an OME is more or less soot free but the energy content is only half that of conventional fossil diesel. OME production route is starting with methanol to DME synthesis and further oxidation to OME.

### **Butanol**

Butanol is an alcohol with four carbon atoms. Of special interest are the two isomers n-Butanol and i-Butanol. Both can be used for blending with gasoline or even as a drop-in replacement in spark ignition engines. n-Butanol can also be used to blend with diesel. There are several benefits for using butanol over ethanol but due to its lower octane rating and butanol not being economically competitive, low research effort was conducted on this topic. Fossil derived butanol uses propane as a feedstock for the oxo synthesis. Biomass derived butanol is produced via fermentation. Unlike ethanol, for butanol fermentation specially bred bacteria have to be used for effective production. A prominent example is the Clostridia bacteria which is used in the ABE process (acetone–butanol–ethanol). Currently, most of the butanol produced is synthesized through chemical processes based on oxo-synthesis, Reppe synthesis or crotonaldehyde hydrogenation [16].

## **6.2 Feedstock Types**

Fossil feedstocks such as crude oil represented a very convenient source for carbon-based compounds for centuries, but their utilization comes at the cost of releasing permanently stored carbon into the

atmosphere. Many alternative fuel pathways still rely on fossil feedstocks, especially for hydrogen production. Non-fossil alternative feedstocks have the advantage of utilizing non-fossil carbon which is captured through different mechanisms in the short or midterm before fuel production. Those feedstocks are not carbon neutral by nature since their production in our current economic system still yields fossil carbon emissions. The carbon that's bound in the feedstock itself though is not affecting the atmospheric carbon balance when reemitted, providing an attractive option for decarbonization efforts in the fuel sector. This chapter gives an overview of feedstocks for alternative fuel production.

### **Fossil Feedstocks**

Those include all feedstocks used for conventional fuel production. Traditional fossil feedstocks still find use in alternative fuel pathways. As part of the fuel pathways evaluated in this study we identified two major applications for fossil feedstocks in synthetic fuel production, being coal gasification and steam methane reforming (SMR). Coal gasification is for instance used by Sasol Synfuels (Pty) Ltd in South Africa to produce syngas and a wide variety of synthetic fuels via subsequent Fischer-Tropsch (FT) synthesis. SMR is also a very mature process to produce syngas which utilizes fossil methane, it is by far the most prominent process for hydrogen production.

This identifies the two major fossil feedstocks relevant to alternative fuel pathways in this study:

- Coal
- Natural Gas

### **Biomass**

Biomass is renewable organic material that is produced by plants and animals. It can be utilized for fuel production in several ways, which will be elaborated in detail in the corresponding section of this study. Biogenic feedstocks need to be categorized further by their content, since the applicable fuel pathways depend on the properties of the feedstock. Table 6-22 gives an overview of common biogenic feedstocks that have been observed in the literature. It is not meant to be exhaustive but gives an overview of the broad variety that biomass yields.

Table 6-2: Biomass classification by content and after RED II.

Classification	Feedstock	For advanced biofuels after RED II
Oil Biomass	Rape Seed	No
	Soya Seed	No
	Palm Fruits	No
	Sunflower Seed	No
	Jatropha	No
	Used cooking Oil/Fats	No
	Animal Fats	No
	Tall Oil	Yes
Sugar Biomass	Sugar Cane	No
	Sugar Beet	No
Starch Biomass	Maize	No
	Wheat	No
	Rye	No
Lignocellulosic Biomass (Woody)	Residues	Yes
	Willow	Yes
	Poplar	Yes
	Eucalyptus	Yes
Lignocellulosic Biomass (Herbaceous)	Straw	No
	Gras	No
Waste Biomass	Manure	Yes
	Biowaste	Yes
	Sludge	Yes
	Maize Silage	Yes
	Mash	Yes
	Wastewater	Yes
	Residues	Yes
	Glycerin	Yes
Black Liquor	Yes	
Algae Biomass	Micro Algae	Yes

Some biogenic feedstocks could be utilized as raw materials or consumer products, while others are considered as waste or byproducts from food, beverage, or wood production. Fuels produced from the latter ones are often referred to as advanced biofuels. Most non-waste biomass implies considerable land occupation, which results in an additional carbon burden on biofuels. This carbon burden emerges from a loss of natural carbon capturing capacity through the transformation of natural land to agricultural acreage. Advanced biofuels tend to have significantly lower LUC implications, as the provision of their feedstocks leads to no other foregone products. LUC emissions depend heavily on the type of plant that's cultivated. This is because different types of crops tend to occupy different types of natural land.

## Hydrogen

Hydrogen is needed for most synthetic fuel pathways such as Fischer-Tropsch synthesis or methanol synthesis, but also HVO production. In addition to its importance as a process input, hydrogen can also be used as a fuel itself. This study does not contain a detailed analysis of hydrogen production, although many hydrogen pathways are embedded in the analyzed fuel pathways. During the literature screening

for this study, some GWP values for hydrogen production were observed. These can be found in the supplementary material but are not elaborated in detail.

Hydrogen from fossil sources is likely to impose high carbon emissions on a fuel pathway while hydrogen from electrolysis via renewable energy has a comparatively small carbon footprint. For electrolytic hydrogen, the main influencing factor concerning GWP is the electricity mix. Another aspect of hydrogen production is water scarcity since electrolysis is dependent on freshwater availability. Water availability in combination with the availability of renewable electricity can lead to a very constrained selection of production locations that are suitable to produce hydrogen with a minimal carbon footprint. Seawater desalination can help to relax some of the location constraints but imposes additional energy consumption on the production pathway.

The most common production process of hydrogen is SMR of natural gas. Hydrogen from natural gas accounts for three quarters of global annual dedicated hydrogen production (making up about 6% of global natural gas use) followed by coal, accounting for about 23% of annual global dedicated hydrogen production (making up about 2% of global coal use). The rather large share of coal is due to its importance in China. [17]

### Carbon Dioxide

Traditionally, most CO<sub>2</sub> was produced from natural gas sweetening, underground sources or washed out of exhaust gas streams from CO<sub>2</sub> intensive production facilities like ammonia plants. In recent years, CO<sub>2</sub> capture has gained more attention. In the context of synthetic fuel production, CO<sub>2</sub> capture is by far the most popular choice for CO<sub>2</sub> sourcing in LCA studies. Especially direct air capture (DAC) is gaining momentum in the recent years as many DAC companies reach commercial scales. Apart from its comparatively higher energy demand, DAC presents a promising option for CO<sub>2</sub> sourcing in the future. This assumption is often supported by the argument that concentrated sources for PSC will become scarcer in a decarbonized future. In addition to the decline of their availability, accessibility is also a drawback of PSC. The availability of concentrated carbon sources in proximity to fuel production facilities could be limiting the integrability of PSC into FPPWs. In terms of availability and flexibility, DAC seems very promising. Carbon capture technologies and their environmental implications will be discussed in section 7.3.

### Electricity

The carbon intensity of an electricity mix is expressed in amounts of CO<sub>2</sub> per unit of energy, most of the time gCO<sub>2</sub>eq/kWh. The value usually reflects a yearly or monthly average since the actual carbon intensity tends to vary over time with the availability of fluctuating renewable energy sources. For many synthetic fuel pathways, this intensity is the deciding factor concerning their carbon footprint. The ongoing decline in the average carbon intensity of most grids will most likely lead to a decline in most synthetic fuels' carbon footprints. There is a significant difference in carbon intensity of grid electricity between regions. In the EU, carbon intensities reach from 8.8 gCO<sub>2</sub>eq/kWh (Sweden) to 774.9 gCO<sub>2</sub>eq/kWh (Estonia) according to an EEA estimate for 2020 [18].

Figure 6-1 shows the development of the carbon intensity of energy in the EU-27. The recent reductions in the carbon intensity are mostly attributable to the shift from fossil energy carriers to renewable energy. If the observed trends continue, a full decarbonization of the energy sector is well possible until 2050. This would be in line with the 55% GHG reduction goal for 2030 (compared to 1990).

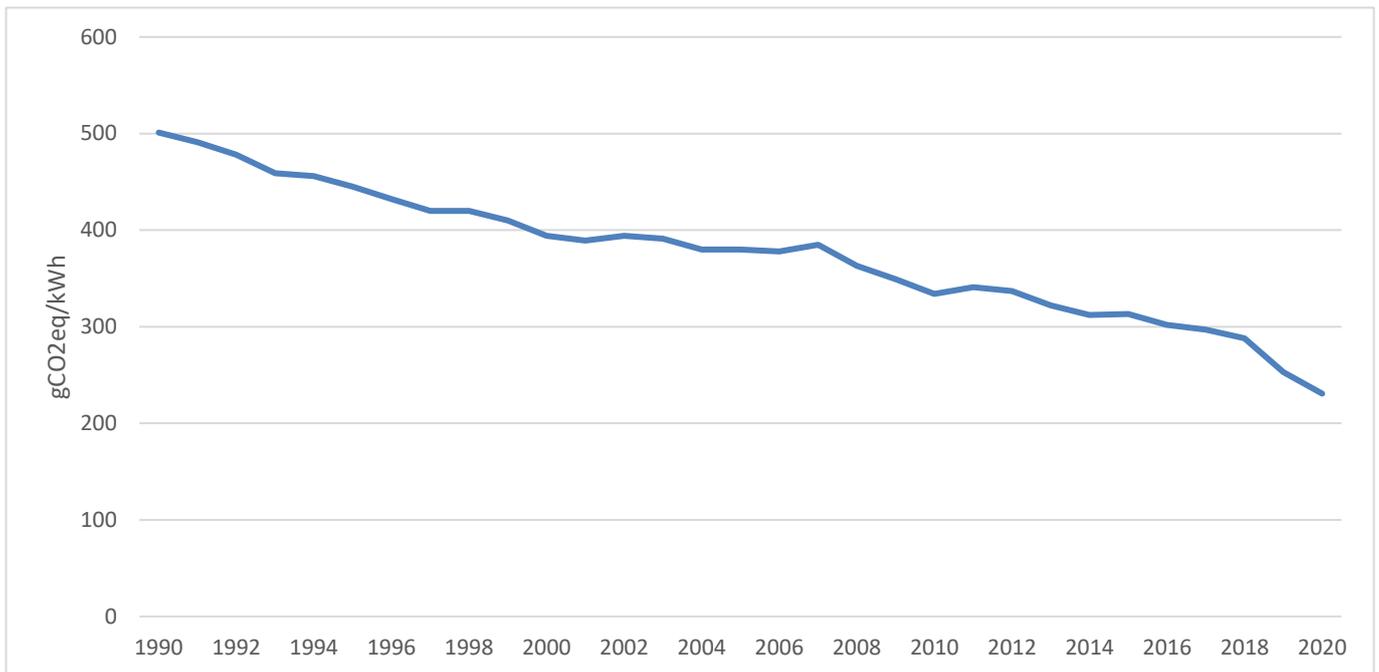


Figure 6-1: Data taken from [18]. Own depiction. Carbon intensity of the EU-27 energy mix

At the time of this estimate, around 34% of the electricity generation was based on renewable sources in the EU-27. From a life cycle perspective, the carbon intensity of renewable energy is not zero even though this is often assumed in literature. Taking emissions from production and decommissioning of renewable energy power plants. **Fehler! Verweisquelle konnte nicht gefunden werden.** shows estimates for the lifecycle carbon intensity of some renewable energy sources.

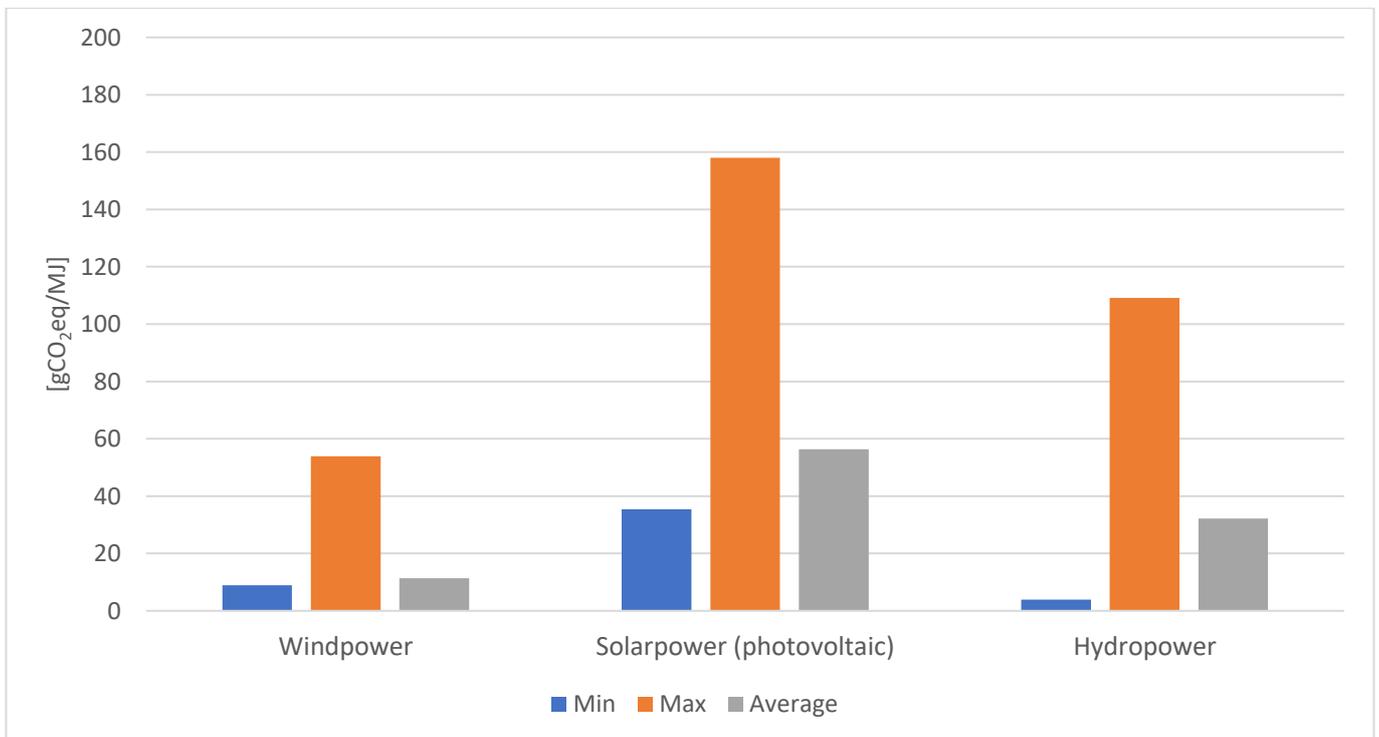


Figure 6-2: Lifecycle carbon intensity estimates for renewable energy sources

The future valuation of lifecycle emissions from renewable energy as well as fluctuations in the availability of natural gas contribute to uncertainties when predicting the carbon intensity development of the European energy mix. It is though very likely that the decline in carbon intensity is prolonged.

### 6.3 Fuel Classification and Production Pathways

The categorization of fuels, especially alternatives to conventional fossil-based fuels is difficult since there is no regulatory framework. Many different categorizations exist, some of them with contradictory classifications. In general, there are three main approaches to categorize fuels. These are: by feedstock, by production process and by chemical composition. Those approaches are often mixed within one classification scheme. A good example is the categorization of synthetic and bio-based fuels. Synthetic fuels are typically defined over the process of creating syngas with subsequent synthesis to a fuel and bio-based fuels are defined over their biomass feedstock. In addition, paraffinic fuels contain bio-based fuels (HVOs) and synthetic fuels (FT fuels). Therefore, many classification systems have the problem of overlapping fuels within their classification systems. This makes it difficult to find a globally shared nomenclature to refer to.

This study provides a classification system (**Fehler! Verweisquelle konnte nicht gefunden werden.**) which attempts to decrease the above mentioned overlapping issues and is based on the classification presented in report [19]. On the top end there is the differentiation between conventional fossil fuels (CFF) and alternative fuels. In a second step alternative fuels are split up into three categories, being hydrogen, gaseous and alternative liquid fuels. Hydrogen is viewed separately to highlight its multifunctionality and importance in a de-fossilized energy system. Alternative liquid fuels are then categorized by their feedstock differentiating between feedstocks of biological origin and feedstocks that consist of syngas components such as CO, CO<sub>2</sub> and H<sub>2</sub>. There is a further need to split up these synthetic fuels into their feedstock derived parts: bio-syn, fossil-syn and non-biomass-syn fuels. Gaseous fuels also contain, besides bio- and synthetic derived fuels, natural gas in all its variations. They could be categorized in a similar manner, but since they only make up a small part of this analysis, they are not further divided. The following chapters will give a detailed overview on each fuel class following the scheme presented in **Fehler! Verweisquelle konnte nicht gefunden werden.**

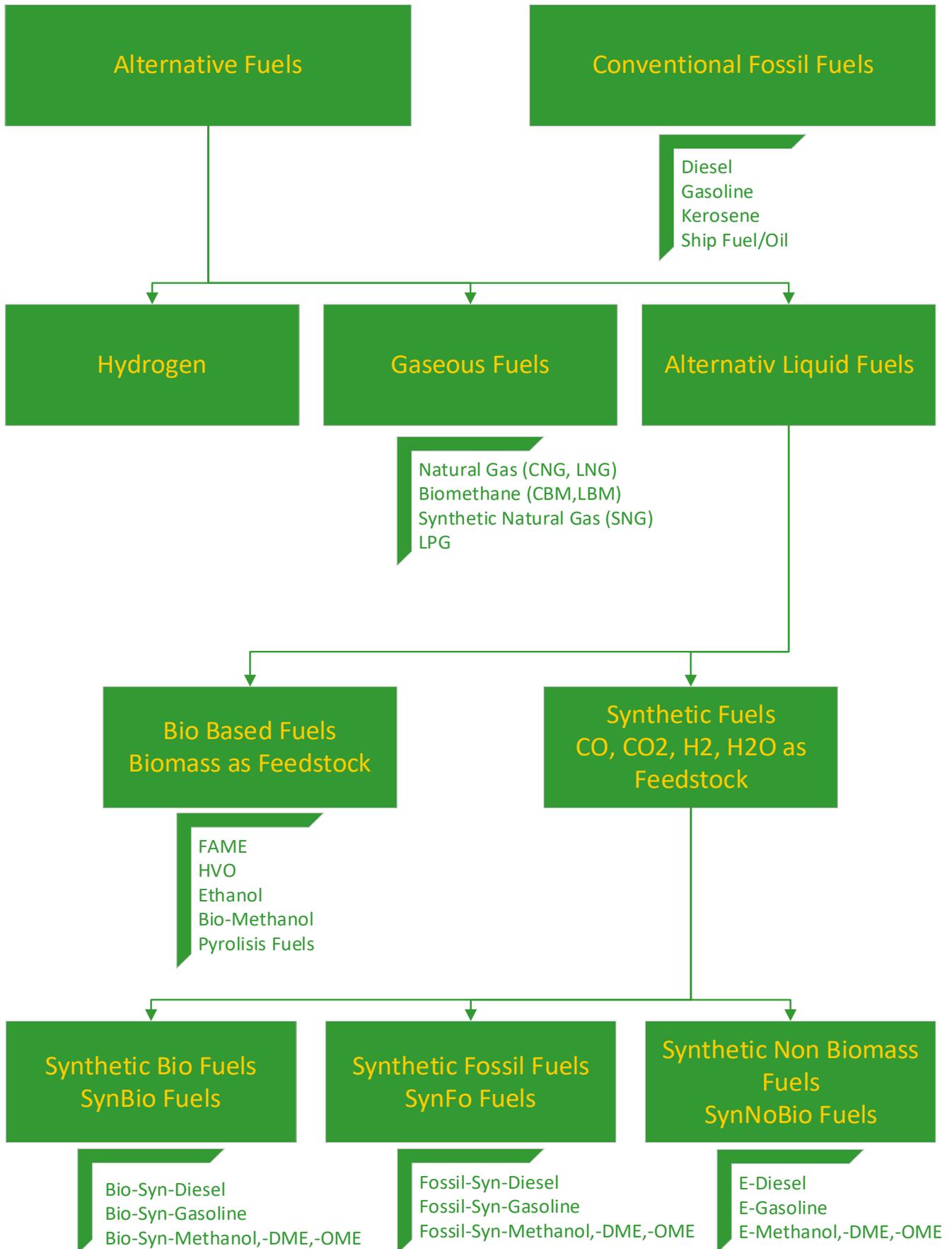


Figure 6-2: Fuel classification scheme.

### 6.3.1 Conventional Fossil Fuels

CFFs are liquid fuels derived from crude oil which is a naturally occurring liquid that exists in underground reservoirs. It is a mixture of hydrocarbons with different chain lengths and constitutions. Also, other compounds such as heteroatoms (sulfur, nitrogen, oxygen, etc.), metals (nickel, vanadium, iron, etc.) and inorganics ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , etc.) are present in crude oil and are separated by a large number of physical or chemical refinery steps. An overview of physical, thermal, and catalytic processes is given in following chapters. [20]

#### Physical Processes

The first step in the refining process is desalting and dehydration where hot water is added to extract contaminants (salt and other impurities). Afterwards the crude oil is separated into fractions by distillation according to the volatility of the components in crude oil. Heavy fractions leaving the crude distillation are further processed in a vacuum distillation. After distillation propan deasphalting is attached to extract "asphaltenic" compounds (which tend to coke formation) of the heavier distillation fractions. The products that are received from distillation do not correspond to the final product distribution. The fuel market desires pure fractions without heteroatoms, gasoline with a high-octane number, diesel with a high cetane number and heavy oils as little as possible. [20]

#### Thermal Processes

In thermal processes heavy feeds, are heated to a sufficiently high temperature to break chemical bonds and producing lighter products. The major techniques are: [20]

- Visbreaking: Reduction in viscosity by relatively mild thermal cracking processes
- Delayed coking: Thermal cracking process with long residence time, where therefore a relatively large amount of coke is produced, which is commonly utilized in electrode production.
- Flexicoking: Process developed by Exxon, to minimize coke production.

#### Catalytic Processes

Catalytic processes are indispensable for increasing the quantity of high-quality gasoline and diesel. Since the amount of gasoline and diesel which is obtained by simple distillation is low, catalytic conversion steps such as hydrocracking or catalytic cracking are carried out. To increase the octane rating processes such as catalytic reforming, or alkylation is desired. The equivalent of the octane number is the cetane number in the case of diesel. For receiving required cetane number of hydrocarbons hydrocracking is commonly used. [20]

The major process to reduce the hydrocarbon chain length is named Fluid Catalytic Cracking (FCC) in fluidized bed reactors. The reaction occurs at temperatures of 500 °C in present of Zeolite-catalyst. The major drawback of this type of reaction is that the Zeolite-catalysis get deactivated through coke formation and must be regenerated. This is done in a separate reactor where the coke from the deactivated catalysis is burned in the present of air at 600 °C. The regenerated catalyst enters the moving bed reactor, and the reaction continues. In addition, FCC is one of the most polluting units in the refinery, because during catalyst regeneration a large amount of sulfur and nitrogen oxides are formed. [21] [20]

Hydrotreating is an efficient method to remove compounds such as, sulfur, nitrogen, oxygen, unsaturated hydrocarbons, and metals with hydrogen. The removal of heteroatoms is named hydrogenolysis which involves the direct scission of carbon-nitrogen, carbon-sulfur, or nitrogen-metal bonds. The hydrogenation reaction where unsaturated hydrocarbons become saturated can be grouped as saturation

of olefins (linear unsaturated hydrocarbon compound) and saturation of aromatics (cyclic unsaturated hydrocarbons compounds). [20]

Hydrocracking can be viewed as combination reaction of catalytic cracking and hydrotreating, but the main objective of hydrocracking is to reduce the molecular size of hydrocarbons and producing straight chain hydrocarbons. The process aims to produce middle distillates such as jet and diesel fuels. In addition, heteroatoms such as nitrogen destroy the acidic character of the cracking-catalyst, therefore hydrodenitrogenation is necessary. [20]

This process of alkylation aims to produce gasoline components with high octane number from low molecular weight alkenes such as propene, butene, isobutene and pentenes. The reaction is catalyzed by strong acids such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and hydrofluoric acid (HF). The temperature for the alkylation process ranges from 0 – 50 °C with pressures from 1 – 30 bar. [20]

Catalytic reforming is next to alkylation a key process to produce gasoline components with high octane number. Straight run naphtha and other feeds ( $\text{C}_6\text{-C}_{11}$ ) are internal rearranged by isomerization, cyclization, and aromatization reactions. [20]

### Blending into desired products

The last step in every oil refinery is the blending step, where the intermediate products are mixed to the optimal combination of desired products. To achieve the tight product specification in form of viscosities, octane numbers, cetane numbers, flashpoints, pour points, etc. blending is carried out. In a typical refinery there are four major blending pools [22]:

- LPG pool where saturated  $\text{C}_3 - \text{C}_4$  hydrocarbons are blended.
- Gasoline pool which counts to the most important blending pool where regular gasoline products such as reformate, light naphtha, alkylate and light cracked naphtha are blended.
- Diesel pool for automotive diesel and heating oil from kerosene.
- Fuel oil pool for fuel oil, heavy fuel oil, and bunker oil which are mainly produced by cracked residues.

### Product distribution

As seen in Figure 6-3 the product distribution between sweet crude oil or heavy fuel oil refined in a “hydroskimming” refinery or complex refinery differs significantly. The quality of crude oil shows a worsening trend and is becoming heavier with higher amounts of impurities, which requires more processing to obtain the same amount and quality of products. In addition, it should be noted that fuel oil is worth less than the unrefined crude oil, where the values of products decrease in the order of gasoline, kerosene/gas oil, crude oil and fuel oil. [20]

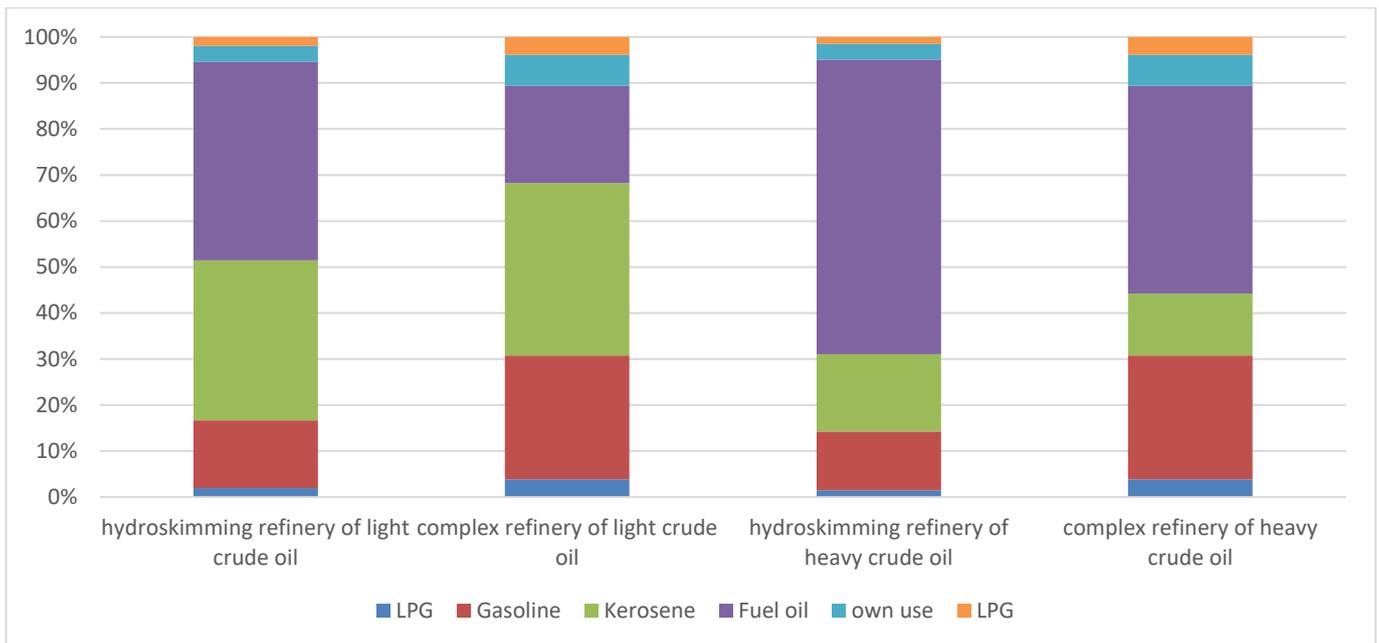


Figure 6-3: product distribution of heavy or sweet crude oil by a simple “hydroskimming” refinery or a complex refinery [20].

### 6.3.2 Hydrogen

Hydrogen is a gaseous energy carrier useable as energy storage in power to gas to power applications, in petrochemical processes for fuel upgrading, Feedstock for SynNoBio fuels and as fuel in FCVs and specialized ICEVs. Although different energy carriers for fuel cells, like ammonia or methanol, are under investigation, hydrogen is still the most promising. Transportation of hydrogen in pipelines for NG is problematic due to “hydrogen embrittlement” effects. Therefore, some regions around the world experiment with NG blended with hydrogen and separation on distribution site. Although OEM’s put a lot of research effort into FCV nowadays, missing hydrogen fueling stations pose the problem of possible restriction of sales.

### 6.3.3 Gaseous Fuels

Gaseous fuels are mainly compressed natural gas (CNG), liquified natural gas (LNG) and LPG derived from fossil feedstocks. Biomass-derived alternatives do exist though and may contribute to the reduction of GHG emissions in the transport sector. Compressed bio methane (CBM) and liquified bio methane (LBM) are mainly obtained by digestion of Biomass. CBM can easily be fed into the already existing gas grids or be liquified for transport. Nowadays NG is already blended with biomethane. The percentage of blending differs from member state to member state. It is possible to produce NG as a synthetic fuel by methanation of syngas, but this pathway seems to be impracticable due to lack of efficiency and high production costs. As mentioned before, gaseous fuels are not further categorized but will be discussed in the following chapters. The production of gaseous fuels is visually summarized in Figure 6-4.

### 6.3.3.1 Natural Gas

Natural gas is a mixture of different gaseous hydrocarbons as seen in Table 6-3.

Table 6-3: Composition of natural gas.

Share in Percentage [>%]	Chemical Name	Chemical Formula
70-90	Methane	CH <sub>4</sub>
	Ethane	C <sub>2</sub> H <sub>6</sub>
0-20	Propane	C <sub>3</sub> H <sub>8</sub>
	Butane	C <sub>4</sub> H <sub>10</sub>
0-8	Carbon Dioxide	CO <sub>2</sub>
0-0.2	Oxygen	O <sub>2</sub>
0-5	Nitrogen	N <sub>2</sub>
0-5	Hydrogen Sulfide	H <sub>2</sub> S
trace	Rare Gases	He, Ne, Xe

#### Process

The process of upgrading of natural gas is less complicated than the processing and refining of crude oil. One of the most important steps in gas processing is the removal of sour gases such as carbon dioxide and hydrogen sulfide. This process is often referred as gas sweetening process and can be carried out with chemical solvents, physical solvents, pressure swing absorption, and separation with membranes. [23] [24]

### 6.3.3.2 Biomethane

Anaerobic digestion is a natural biological process that occurs by exclusion of oxygen and converts organic matter such as agriculture residues, municipal/industrial biowaste and animal manure into biogas. The production of biogas via anaerobic digestion forms a gas mixture composed mainly of methane (50-75%) and carbon dioxide (25-50%). Depending on the organic matter substrate being digested, minor amounts of hydrogen sulfide (<0.8%) and ammonia (<1%) are formed. The process of digestion is a four-step process (hydrolysis, acidogenesis, acetogenesis and methanogenesis) carried out by microorganisms. It can be performed by using mesophilic or thermophilic conditions. Thermophilic treatment is operated optimally between 49 °C and 57 °C up to 70 °C, whereas mesophilic treatment is operating at its optimum between 30 °C and 35 °C. According to the literature, 90% of anaerobe digester uses mesophilic digestion. [25]

#### Pretreatment

The goal of pretreatment is to improve the feedstock accessibility for microorganisms by increasing the surface area, biomass porosity, decrystallization and solubilization. The efficiency of pretreatment can be expressed as an increase in the methane/biogas yield. Pretreatment technologies can be differentiated into mechanical such as ultrasonic, microwave, electrokinetic and high-pressure homogenization, thermal at high and low temperatures, chemical such as acidic, alkali, ozonation and Fe(II)-activated persulfate oxidation, and biological in temperature-phased anaerobic digestion and microbial electrolysis. In addition, due to the wide variety of feedstock that can be used for anaerobic digestion the pretreatment has to be adapted to the feedstock. For example, if agriculture waste is used, which is mainly composed of cellulose, hemicellulose, and lignin it is resistance to microbiological degradation and oxidation. Thus

the pretreatment is mostly a combination of elevated temperature and chemical treatment or a hybrid treatment of mechanical and thermal. [25]

### Hydrolysis

The first step is the depolymerization of organic matter. During hydrolysis insoluble substrates such as polysaccharides, fats, proteins are hydrolyzed into smaller, soluble units by a large number of hydrolytic microorganisms containing different hydrolyzing enzymes such as cellulase, cellobiase, xylanase, amylase, protease, lipase. [26]

### Acidogenesis

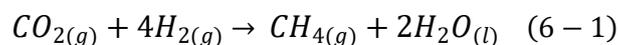
Acidogenesis is usually the fastest reaction in anaerobic digestion. During acidification of short-chain sugars, long-chain fatty acids and amino acids resulting from the degradation of complex organic matter from hydrolyzing step, fermentative microorganisms are used to produce short-chain organic acids, alcohols, hydrogen, and carbon dioxide. Due to the transition from organic materials to organic acids a drop in pH-value occurs, which is beneficial acidogenic and acetogenic bacteria that prefer an acidic environment in the pH range of 4.5 – 5.5. [26]

### Acetogenesis

Acetogenic bacteria are strict anaerobes and have an optimum pH of around 5.5 – 6. They are growing 10 times slower than acidogenesis bacteria and are extremely sensitive to oxygen, fluctuations in organic loadings and environmental changes. Those microorganisms convert ethanol or propionate into acetate, which can be directly converted into methane and carbon dioxide. They have the ability to couple hydrogen gas with carbon dioxide to acetate. [26]

### Methanogenesis

Methane is produced as a metabolic byproduct by a methanogenic microorganism that belongs to Archaea. Those microorganisms metabolize  $H_2/CO_2$ , methanoate, methylated  $C_1$  compounds or acetate as energy and carbon sources. Methane production, which is somewhat an unusual type of metabolism occurs in two ways either by cleavage of acetic acid molecules to generate carbon dioxide and methane or by reducing carbon dioxide with hydrogen. Those two reactions paths are viewable in formula 6 - 1 and 6 - 2. [26]

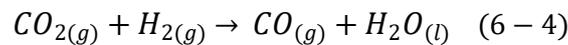
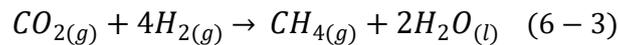


### Posttreatment and Biogas Upgrading

For biogas to be used in the transport sector, carbon dioxide and methane must be separated with the aim of achieving a natural gas specification above 95 vol% methane content. Conventional upgrading technologies including, membrane separation, absorption methods such as scrubbing with water or chemicals, pressure swing adsorption with zeolites, activated carbon or carbon molecular sieves and cryogenic separation. The organic matter residues are mainly used as fertilizers. [27]

#### 6.3.3.3 Synthetic Methane

The approach of thermo-catalytic conversion. Methanation is often mentioned as Sabatier process according to its discoverer Paul Sabatier, where a catalytic conversion of  $CO_2$  in presence of molecular hydrogen into  $CH_4$ , which is illustrated in equation 6-3, occur.



A suitable catalyst must be applied to promote selectively CO<sub>2</sub> methanation, because the main side product (CO) will be formed as seen in equation 6-4. For the simplest case, the reaction between CO<sub>2</sub> and H<sub>2</sub> to CH<sub>4</sub> the methanation reaction can be described as follows [28]:

- Carbon dioxide gas as well as hydrogen gas will be adsorbed on the catalyst surface by chemisorption and create active species
- The adsorbed compounds react and create methane and water.
- Desorption takes place where the products are dissociated off the catalyst surface.

Catalysts used in methanation reaction are usually nickel based catalyst, but manganese-based as well as noble-metal-based catalyst are deployed in methanation. The conversion of H<sub>2</sub> and CO<sub>2</sub> take place at temperatures in the range of 300 – 550 °C and pressures from 1 to 100 bar. In literature there are three major process concepts: fixed bed methanation, fluidized bed methanation, and three phase methanation. [28] Biogas upgrading for the use in the transport sector is the same as mentioned in posttreatment and biogas upgrading in anaerobe digestion.

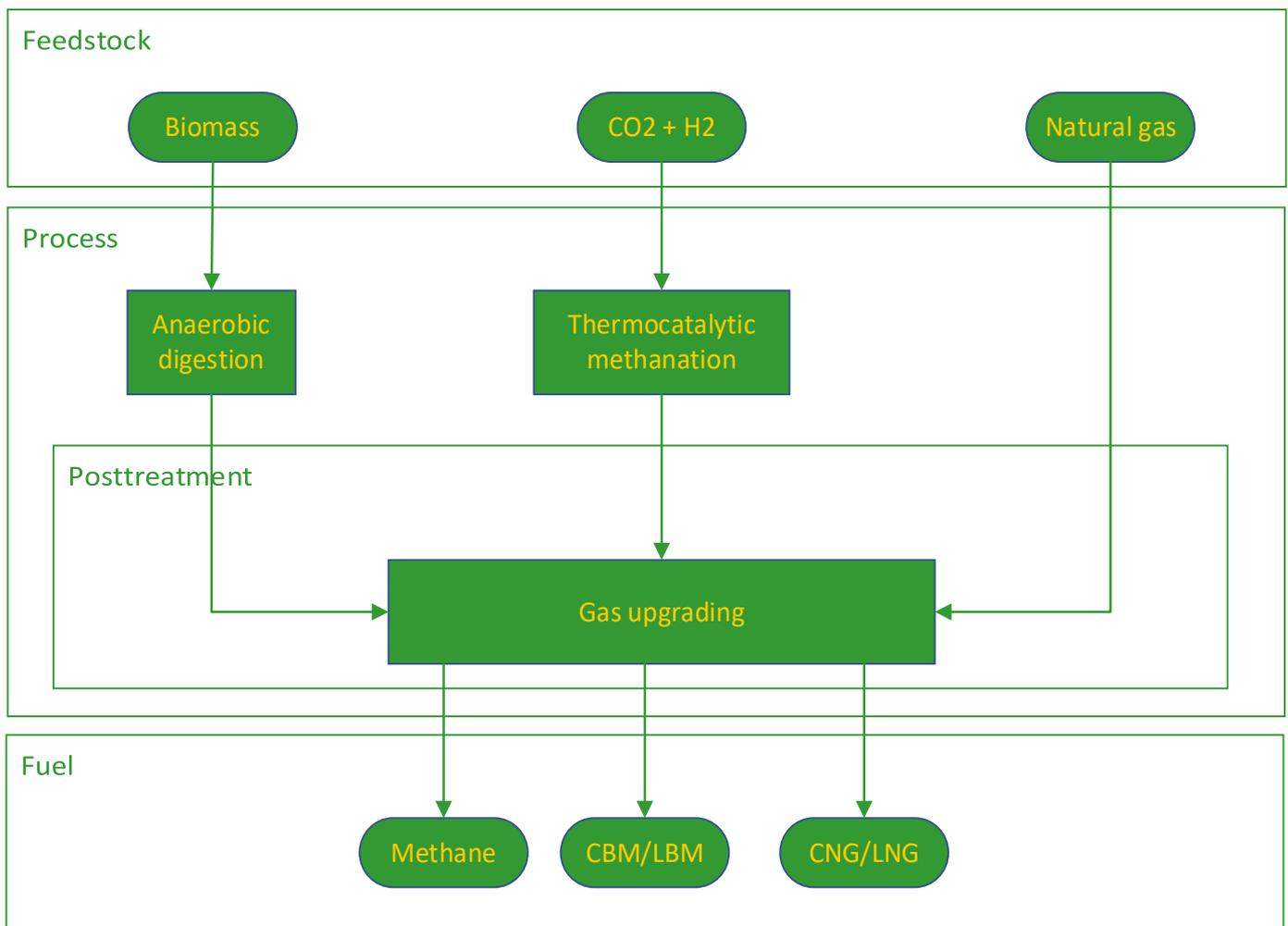


Figure 6-4: Production pathway scheme of gaseous fuel.

### 6.3.4 Bio-based Fuels

Today, biomass-derived fuels are commonly used as blends in traditional fuels. FAME and HVO are usually blended with Diesel, while Ethanol is blended with Gasoline. To use FAME or Ethanol as a 100 % replacement in conventional combustion engines, minor changes to the vehicle have to be applied. On the other hand, HVO could theoretically be used as a drop-in replacement but regarding the regulations for Diesel in the EN590, HVO has a too low density.

Table 6-4: Overview on biomass derived fuels.

Fuel Name	Feedstock	Pretreatment	Intermediate Process	Main Process	TRL	LHV [MJ/kg]
<b>FAME</b>	Oil Biomass	Oil Extraction	-	Trans-esterification	8-9	37.2
<b>HVO</b>	Oil Biomass	Oil Extraction	-	Hydrotreatment Hydrocracking	9	44
<b>Ethanol</b>	Starch Biomass	Glucose Extraction	-	Fermentation	9	26.8
<b>Ethanol</b>	Sugar Biomass	Dry- Wet milling	Hydrolysis	Fermentation	9	26.8
<b>Ethanol</b>	Lignocellulosic Biomass	Milling	Hydrolysis	Fermentation	8	26.8
<b>Pyrolysis Diesel</b>	Lignocellulosic Biomass	-	Pyrolysis	Distillation	6	43.1
<b>Pyrolysis Gasoline</b>	Lignocellulosic Biomass	-	Pyrolysis	Distillation	6	43.2
<b>HTL- Diesel</b>	Lignocellulosic Biomass	-	Hydrothermal liquification (HTL)	Distillation	4	43.1

There is an ongoing discussion on which bio-based fuels are considered advanced (also often referred to as second-generation bio-based fuels). This categorization is done either via the final molecule or the feedstock used. Advanced bio-based fuels typically use feedstocks that do not compete with biomass for the food industry. EU's renewable energy directive (RED) defines which feedstocks fall under this category. This study does not aim to provide deeper insights into that topic, since the whole topic is under controversial discussion and there is no clear statement yet to be made.

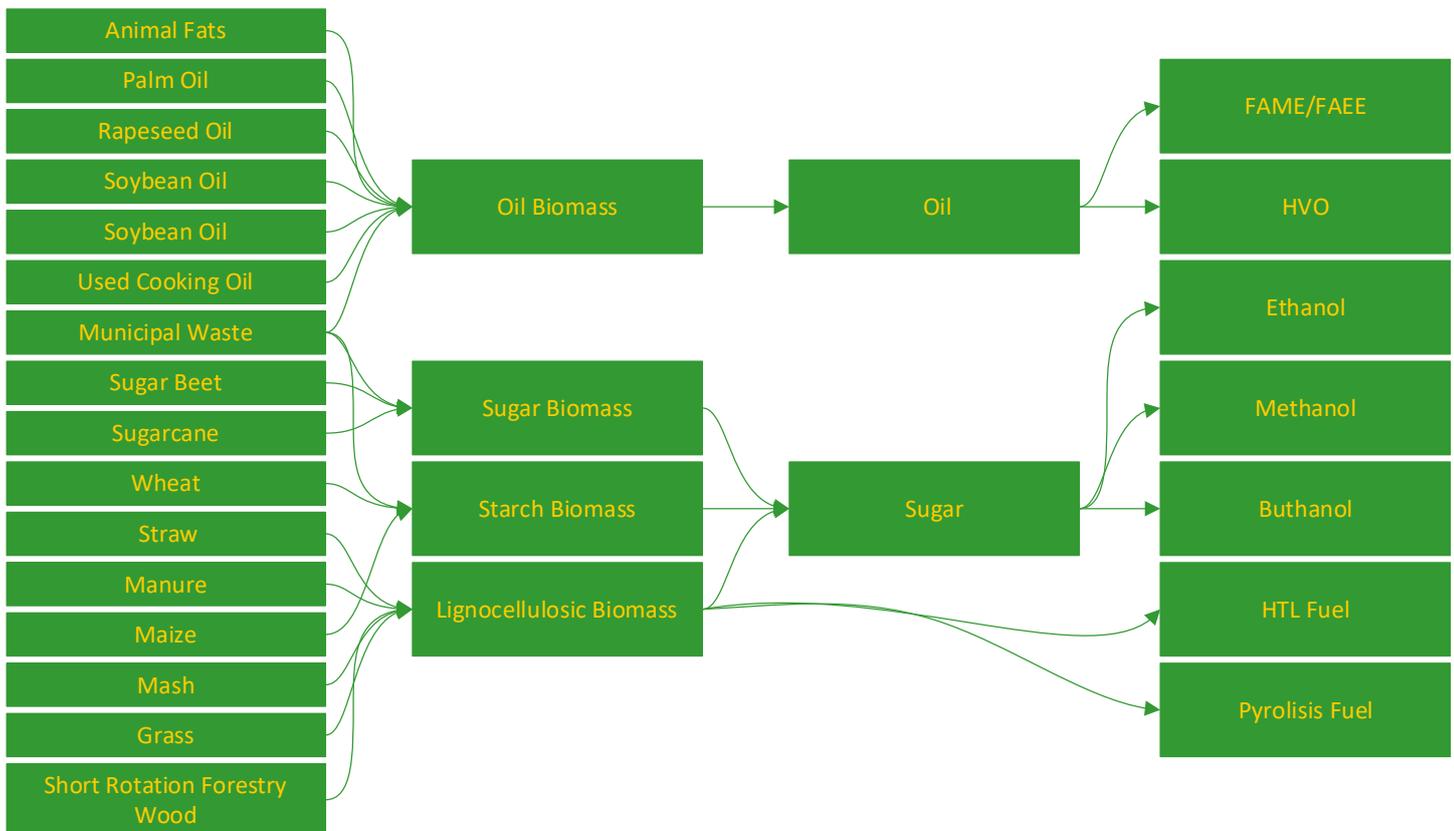


Figure 6-5: Pathways for different biomass feedstock types to their possible fuels.

Figure 6-5 gives an overview on bio-based fuels and their possible corresponding feedstocks. Production pathways of bio-based fuels will be discussed in the following chapters.

### 6.3.4.1 FAME

FAME (fatty acid methyl ester) is produced by the transesterification process from fatty acids with methanol. The physical properties are similar to conventional diesel therefore it is often named biodiesel. The main feedstock that is used for FAME production is oil biomass such as oilseed (rape, sunflower, soy, palm) used cooking oil or waste animal fat. Chemically, fats are a mixture of many triglycerides where all three hydroxy groups of the glycerol are esterified with fatty acids. The transesterification process aims to split the connection between the glycerol and the fatty acid to produce free fatty acids (FFAs) which are further connected with the alcohol compound. This chemical reaction is illustrated in Figure 6-6. If ethanol is used as an alcohol compound the resulting product is a fatty acid ethyl ester. Methanol is preferred, due to its low cost and physiochemical advantages (polar compound and shortest chain alcohol [29]), but the reaction is feasible with longer alcohols such as propanol and butanol. The catalyst that is used for the process can be alkaline, acidic, or enzymatic. Due to the rigorous reaction condition and the enzyme activity loss of the enzymatic catalyzed reaction is not used in large-scale commercial biodiesel production facilities. The acid-catalyzed transesterification is not that popular, because it is 4000 times slower than the base-catalyzed reaction but find application in the pretreatment of oils with a high FFA concentration. There is also the possibility of transesterification under supercritical conditions, where the non-polar triglycerides and the polar alcohol becomes a single homogenous phase. Under normal conditions, those two components form a two-phase mixture that has to be stirred vigorously for several hours. At supercritical conditions, the reaction is completed in minutes. The drawback of this process is the high cost of apparatus due to the high temperature and pressure, which are not viable in large-scale

practice in industry. According to the literature, most biodiesel production plants are using an alkaline catalyst (sodium or potassium hydroxide). [61] [30]

### Pretreatment

The pretreatment of alkaline catalyzed esterification consists of an acid catalyzed esterification step to reduce the amount of FFA in the oil. The concentration of FFA changes depending on the feedstock that is used. Used cooking oil has a large amount of FFAs. Owing to the high temperature of the oil and the water content, that is transferred from the fried food hydrolyses the triglyceride. Other contamination such as soluble compounds, fried food residues and impurities must be removed in order to enhance the quality of fuel. Vegetable oil has a lower concentration of FFA but it always depends on the quality of the raw material, collecting condition, storage and age of the oil. If the FFA level exceeds 0.5 wt%, saponification will hinder the separation of the esters and glycerol which will lead to lower yield. A possible production pathway with an acid catalyzed pretreatment for removing FFA content is viewable in Figure 6-6. [61] [30]

### Process

In the alkaline catalyzed reaction pathway, the catalyst mostly KOH, NaOH is dissolved into the methanol. The methanol-catalyst solution is then pumped into the oil and is stirred vigorously at ambient temperature and pressure. Transesterification is an equilibrium reaction, to shift the reaction equilibrium to the product side an excess of methanol is used to produce more methyl esters. A successful transesterification reaction produces two phases. An ester phase and a crude glycerol phase. After phase separation the heavier glycerol can be collected at the bottom. The ester phase is washed with water till it becomes clear. [61] [30]

### Posttreatment

In order to meet the European standard EN14214 for biodiesel the ester-solution is finally purified. In the literature there are many varieties to purify the biodiesel like vacuum drying, acidulation steps, vacuum distillation. All these steps aim to reduce the water, methanol, and catalyst content. The wastewater undergoes a distillation to recover methanol, which was used in an excess as mentioned before. [61] [30]

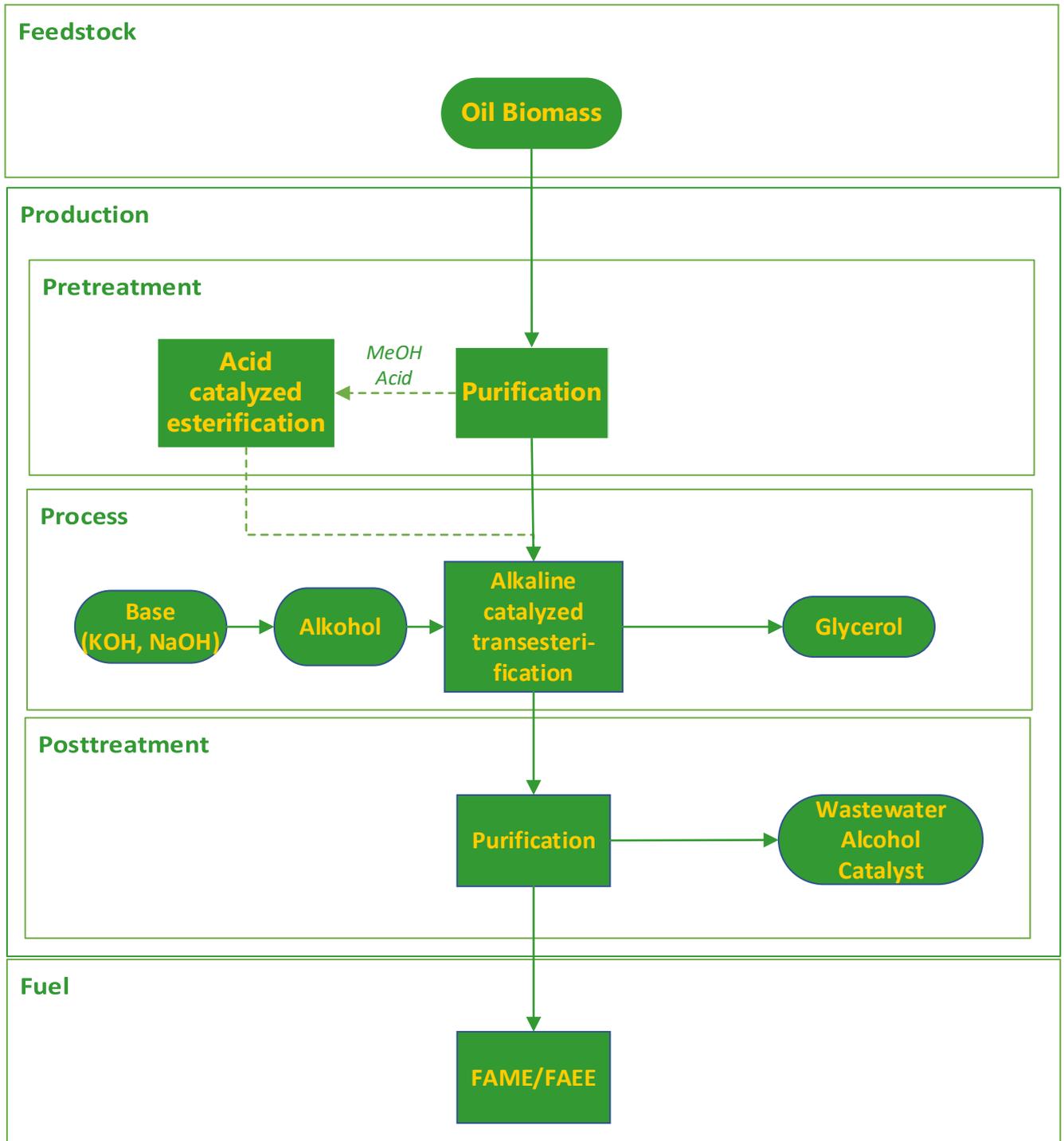


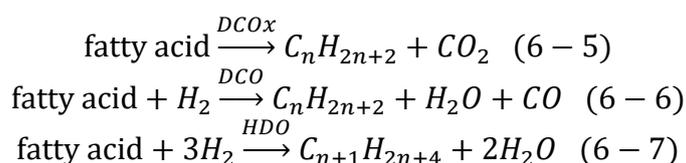
Figure 6-6: Production pathway scheme of FAME.

### 6.3.4.2 HVO

Hydrotreating catalysis is becoming a promising alternative to transesterification for the production of biofuels namely hydrotreated-vegetable-oil (HVO). As feedstock oleaginous biomass is used such as vegetable oil, waste cooking oil or animal fat. After harvesting, the oil is extracted through pressing and can be transported to a HVO production plant. HVO production involves several different processes, such as hydrogenation of the triglycerides, cracking and isomerization of the obtained paraffinic chains to improve combustion properties.

## Hydrotreating Process

The hydrotreating process consists of various catalytic reaction mechanisms in the presence of hydrogen. The hydrogen that is used in the HVO production today mainly comes from fossil source [31]. First the unsaturated carbon-carbon double bonds get saturated in a process that is called hydrogenation. The hydrogenation also forms FFAs, diglycerides and monoglycerides. After the saturation more hydrogen is added which causes braking of the glycerol compound and forming FFAs and propane. The removal of the carboxylic acid can happen in three different ways: hydrodeoxygenation (HDO), decarboxylation (DCOx) or decarbonylation (DCO). All reaction possibilities are viewable in formular 6 - 5; 6 - 6; 6 - 7. In the hydrodeoxygenation pathway, hydrogen reacts with the carboxylic acid and produce two moles of water and a hydrocarbon chain with the same number of carbon atoms as the fatty acid chain. In the decarboxylation route, CO<sub>2</sub> and a hydrocarbon chain with one carbon less is formed. In the decarbonylation reaction there is also a hydrocarbon with one carbon atom less produced as well as one mole of CO and one mole of water. The optimal catalytic pathway for hydrotreating is an economic question and depends on the desired products and the price of hydrogen. But all reactions have the same goal, to remove the oxygen from the fatty acid and producing saturated straight chain hydrocarbons. [32]



Straight chain alkanes are ideal as diesel fuel, regarding to their high cetane number, but the large number of n-alkanes increases the cloud point. To prevent this isomerization may be desired. If shorter alkanes are desired cracking can be done. A full possible fuel production pathway for the hydrotreatment of oil biomass is shown in Figure 6-7. During the whole process, there has been two types of catalyst reported in the literature: conventional bimetallic sulfide catalyst such as NiMoS<sub>2</sub>, CoMoS<sub>2</sub> and NiWS<sub>2</sub> supported on Al<sub>2</sub>O<sub>3</sub> and monometallic catalyst such as Ni, Pd, Pt, Rh. The conversion usually takes place at high temperature between 290 – 300 °C and high pressure in the range between 30 – 200 bar. [32] [31]

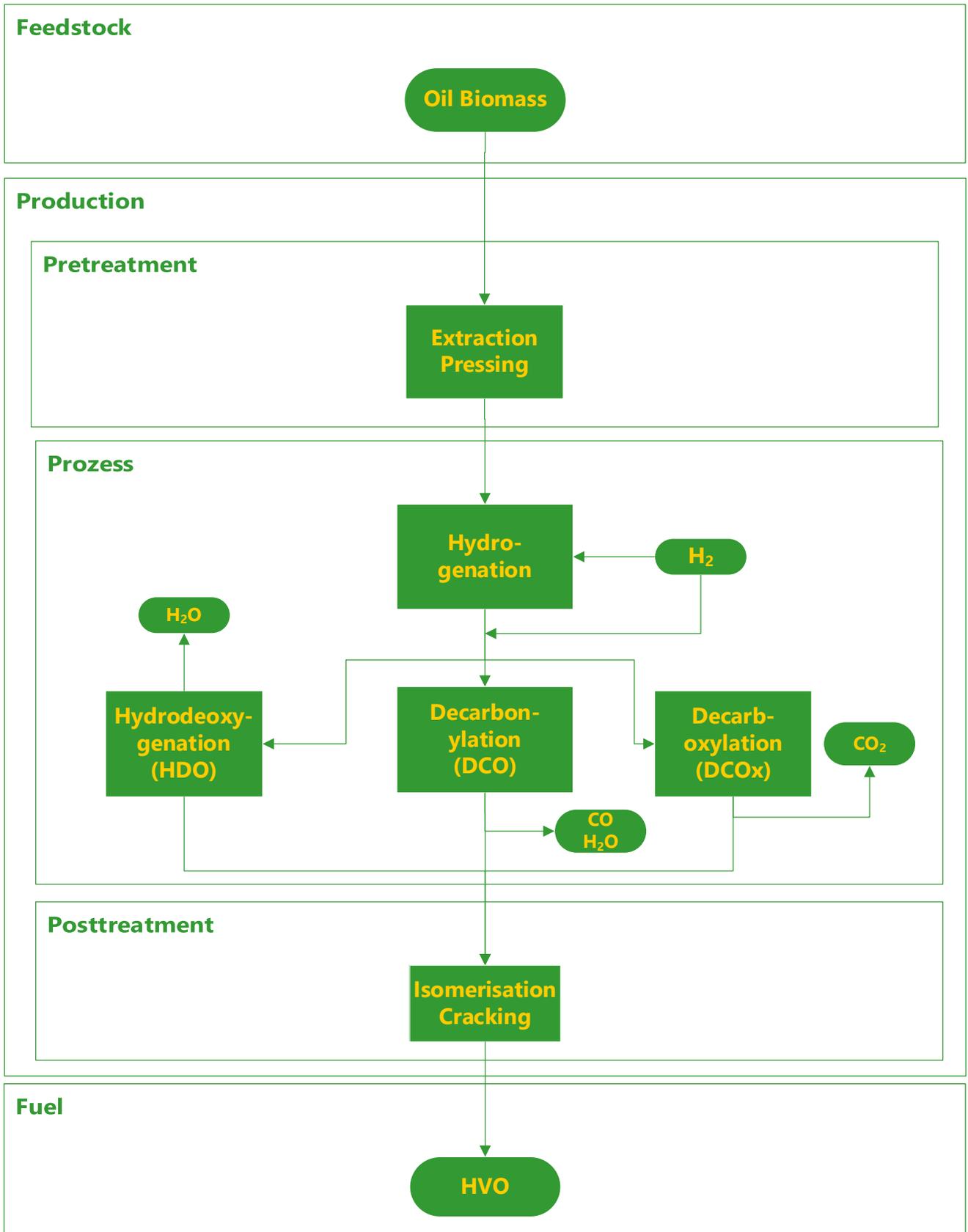


Figure 6-7: Production pathway scheme of Hydrotreated Vegetable Oil (HVO).

### 6.3.4.3 Ethanol

The production of ethanol is a biochemical pathway where sugar is extracted and afterward fermented with microorganisms. The feedstocks are sugar or starch containing biomass or lignocellulosic materials. If sugar or starch containing biomass is used as feedstock for ethanol production, there is the dilemma between food vs fuel. The conversion of lignocellulose into exploitable sugar is more complicated than starch into usable sugar since those polysaccharides are more stable than starch. As seen in Figure 6-8 all three process pathways are the same, but they all differ in the pretreatment.

#### Pretreatment of Sugar Containing Biomass

The mostly used feedstock for ethanol production from sugar biomass is sugar beet or sugar cane. After milling there are two major possibilities for the pretreatment of those primary materials. At first the sugar can be elutriated with hot water, or after the milling process the sugar containing liquid gets pressed off the residue. The residue from sugar beet is called molasse and the residue from sugar cane is named bagasse. Those are typically utilized in steam generators for heat and electricity generation but can also be used as animal food. [33]

#### Pretreatment of Starch Containing Biomass

The milling process is possible in different ways such as dry or wet milling. There is also a more complex milling step, where it is possible to grind the starch containing material in a way that some of the corn ingredients like bran, gluten and germ oil can be separated [33]. The starch containing material which consists of long strands  $\alpha(1-4)$  and  $\alpha(1-6)$  glycosidic bonds, blended with water and heated up to 90 °C in a process which is called mashing. During mashing, enzymes are utilized to hydrolyze those glycosidic bonds into smaller branches of glucose and finally into the representing monosaccharides. [33]

#### Pretreatment of Lignocelluloses

Lignocellulose is a mixture made from carbohydrate polymers such as cellulose, hemicellulose and an aromatic polymer named lignin. Cellulose is built up of linear chains of a disaccharide named cellobiose, where two glucose molecules are connected by  $\beta(1-4)$  glycosidic bond. Hemicellulose consists of four different pentose heteropolymers, such as xylose, mannose, glucose, and galactose. Lignin is a complex macromolecule which cannot be saccharified, but it can be combusted for heat generation or gasified. The main pretreatment which is illustrated in the literature for ethanol production is to hydrolyze the biomass, followed by enzymatic saccharification. In enzymatic saccharification, enzymes break down cellulose fibers into the monomer cellobiose and soluble glucose-oligomers and glucose molecules. The pentoses of the hemicellulose are as well broken down enzymatically. [34]

#### Process

As mentioned above, the production of ethanol from the three different feedstocks differs only in the pretreatment with the goal to produce a sugar-containing solution, which can be fermented and afterward distilled. For fermentation, microorganisms like yeast, bacteria or fungi are used. For example, under anaerobe conditions yeast generate from one-kilogram sugar 0.51 kg ethanol and 0.49 kg CO<sub>2</sub> but there are also some small amounts of higher alcohols as side products [33]. According to the literature the ideal temperature is 32 °C, but it always depends on the microorganism species that is used [33]. After all substrate is fermented, the solution has to be separated into water, ethanol and side products like combustible solids and higher alcohols. The separation takes place by distillation in a rectification column. The remaining water is removed in the posttreatment. The water that is accumulated through the distillation is mostly recovered via wastewater treatment and can be reused. The residues that are left is

deployed in agriculture as animal feedstuff or as fertilizer. Lignin is mostly combusted for heat generation as mentioned in the pretreatment. [34] [35] [33]

### Posttreatment

In the final step, the drying process of ethanol occurs. Molecular sieves are commonly used to get rid of the remaining water. The specification for ethanol as fuel is a maximum of 0.5 m% H<sub>2</sub>O. [33]

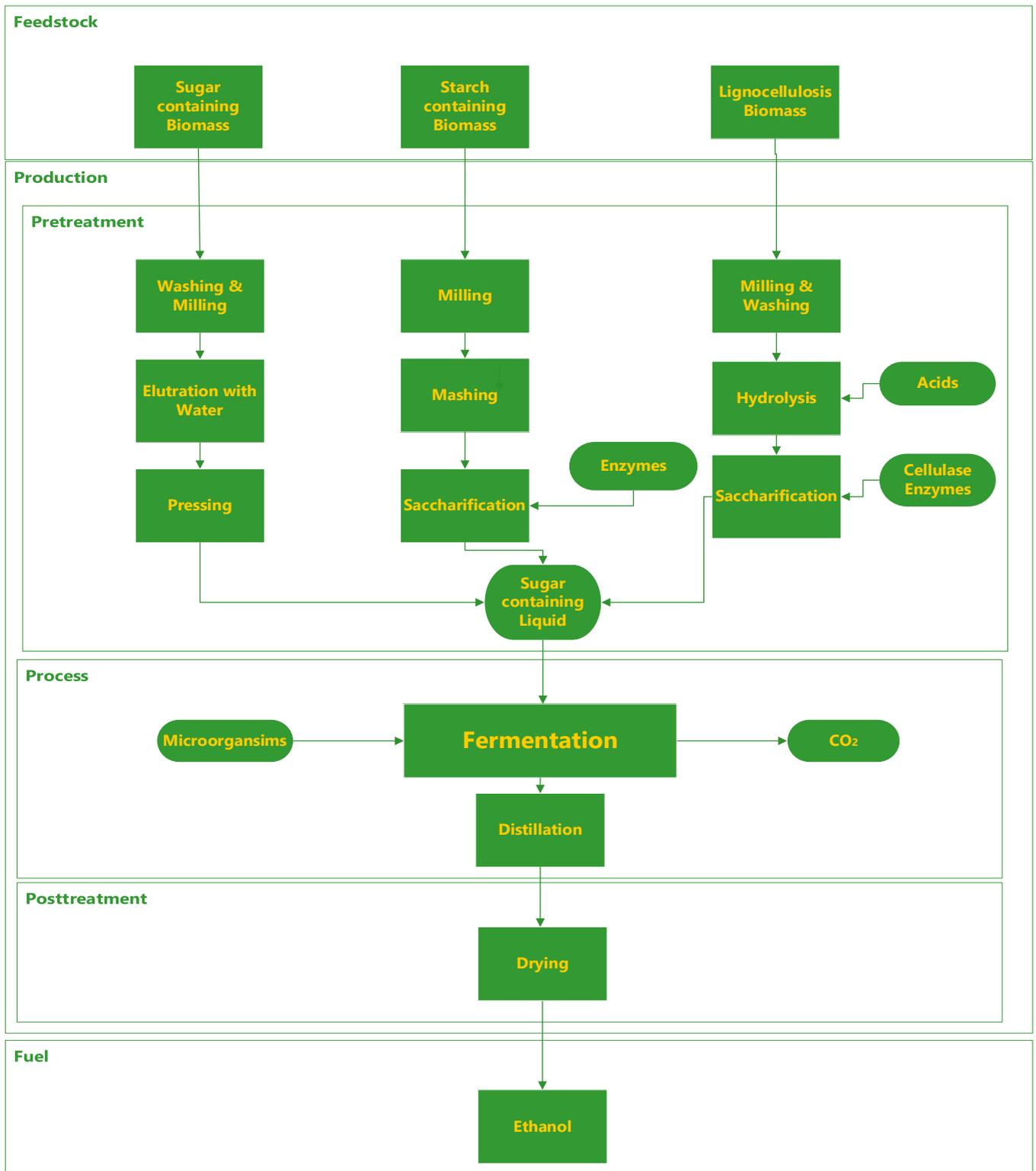


Figure 6-8: production pathway scheme of ethanol

### 6.3.4.4 Pyrolysis Fuel

Pyrolysis refers to the thermal breakdown of biomass (mostly lignocellulosic biomass) to liquid (bio-oil), carbon solids such as char or biochar and a mixture of non-condensable gases at elevated temperatures. Gases results when the process temperatures are high with long residence times, and long vapor residence times. Lower process temperatures lead to char production. For bio-oil production short vapor residence time and lower temperatures are favored. The process mode, process condition and resulting product distribution a summarized in Table 6-5. Several factors affect biomass pyrolysis performance, such as feedstock type, temperature and heating rate, volatiles residence time and pressure, particle size, shape and orientation, reactor configuration, catalysts, additives, and physicochemical properties like thermal conductivity, permeability and density, specific heat capacity and heat of reaction, particle shrinkage as well as the moisture content. [36]

Table 6-5: product distribution at different pyrolysis conditions [36].

Pyrolysis Mode	Conditions	Product Distribution [wt%]		
		Liquid	Solid	Gas
<b>Fast</b>	500 °C hot vapor residence time, <2s	75	12	13
<b>Intermediate</b>	500 °C Moderate hot vapor time, 5-30s	50 (2 phases)	25	25
<b>Slow</b>	400 °C Long hot vapor residence time, hours to days	30 (2 phases)	35	35
<b>Gasification</b>	750-900 °C moderate hot vapor time, >5s	3	1	96
<b>Torrefacation</b>	280 °C solid residence time, 10-60 min	0	80	20

#### Bio-oil

Bio-oil is a dark brown organic liquid formed by simultaneous fragmentation and depolymerization of lignocellulose in fast pyrolysis of biomass. The composition of bio-oil generally contains a high content of water and many different organic compounds such as acids, alcohols, ketones, furans, phenols, ethers, esters, sugars, aldehydes, alkenes, and oxygenated compounds. The properties of bio-oil are dependent on a lot of parameters like heating rate in the reactor, residence time inside the reactor, biomass particle size, type of biomass that is used and temperature. [37] [36]

#### Char

Char is the solid product of the biomass pyrolysis process. Depending on the composition of biomass and process condition, char has different chemical and physical properties. For example, its carbon content ranges from 53 wt% to 93 wt%. The yield and heating value also diversify in a wide range (20 – 24 MJ/kg) [37]. Char is supplied as a soil amendment including carbon sequestration, soil fertility improvement and pollution remediation. It is also used in catalytic utilization or energy storage. [37] [36]

#### Pyrolytic Gas

The main gases that are produced in the pyrolysis of biomass are carbon dioxide, carbon monoxide, hydrogen, methane, ethane, ethylene, propane, sulfur oxides, nitrogen oxides and ammonia. Carbon monoxide and dioxide are mainly produced by the decomposition and the reforming of carboxyl and carbonyl groups. Lighter carbons are originated from the decomposition of methoxy and methylene bonds. Hydrogen is the result of reforming the decomposition of C-H bonds and aromatics. [37] [36]

#### Pretreatment

To enhance the efficiency of pyrolysis, the biomass needs to be pretreated. Pretreatment is preformed [37] [36]

- Physically: adjustment of biomass particle size
- Chemically: removal of negative influencing compounds
- Hydrothermal: increasing energy content of biomass

### Process

As seen in Table 6-5 fast pyrolysis produces the highest liquid content. Slow and intermediate pyrolysis focus on the production of solid char with liquids and gases as by-products. Since liquid fuels are primarily wanted as transport fuels, fast pyrolysis is the reaction pathway of choice for the production of liquid bio-based fuels. Fast pyrolysis operates at a moderate temperature around 500 °C and is characterized by a high heating rate, short hot vapor residence time and short reaction time. After swiftly degradation of biomass to vapor and aerosols, the vapor is cooled and condensed into a dark brown homogenous liquid. As seen in Table 6-6 the major chemical constituents of fast pyrolysis liquid are water, aldehydes, carboxylic acids carbohydrates phenols, alcohols, and ketones. [38] [37]

Table 6-6: Chemical product distribution of fast pyrolysis [36]

Major Components	Examples	Mass (wt%)
Water		20-30
Lignin fragments		15-30
Aldehydes	formaldehydes, acetaldehydes, hydroxyacetaldehyde, glyoxal	10-20
Carboxylic acids	formic acid, propionic acid, butyric acid, pentanoic acid, glycolic acid	10-15
Carbohydrates	cellobiose, $\alpha$ - $\beta$ -levoglucosan, oligosaccharides, 1,6-anhydroglucofuranose	5-10
Phenols	phenol, cresol, guaiacols, syringol	2-5
Furfurals		1-4
Alcohols	methanol, ethanol	2-5
Ketones	hydroxyacetone, cyclopentanone	1-5

### Posttreatment (Bio-oil Upgrading)

Due to numerous oxygenated compounds, the bio-oil is highly acidic, corrosive, and unstable. This means that the bio-oil quality has to be improved before it useable as a fuel. For upgrading bio-oil several physical methods such as filtration, solvent addition, emulsification as catalytic and chemical methods such as hydrotreating, hydrocracking, esterification, ketonisation, and zeolite cracking are possible. For industrial fuel production via pyrolysis, hydrotreating followed by hydrocracking and zeolite cracking are favored. The stable oil is then separated into light and heavy fractions via distillation. The heavy fractions with a boiling point above 350 °C are sent to the hydrocracker to completely convert the oil to gasoline and diesel. The whole process is illustrated in Figure . [37]

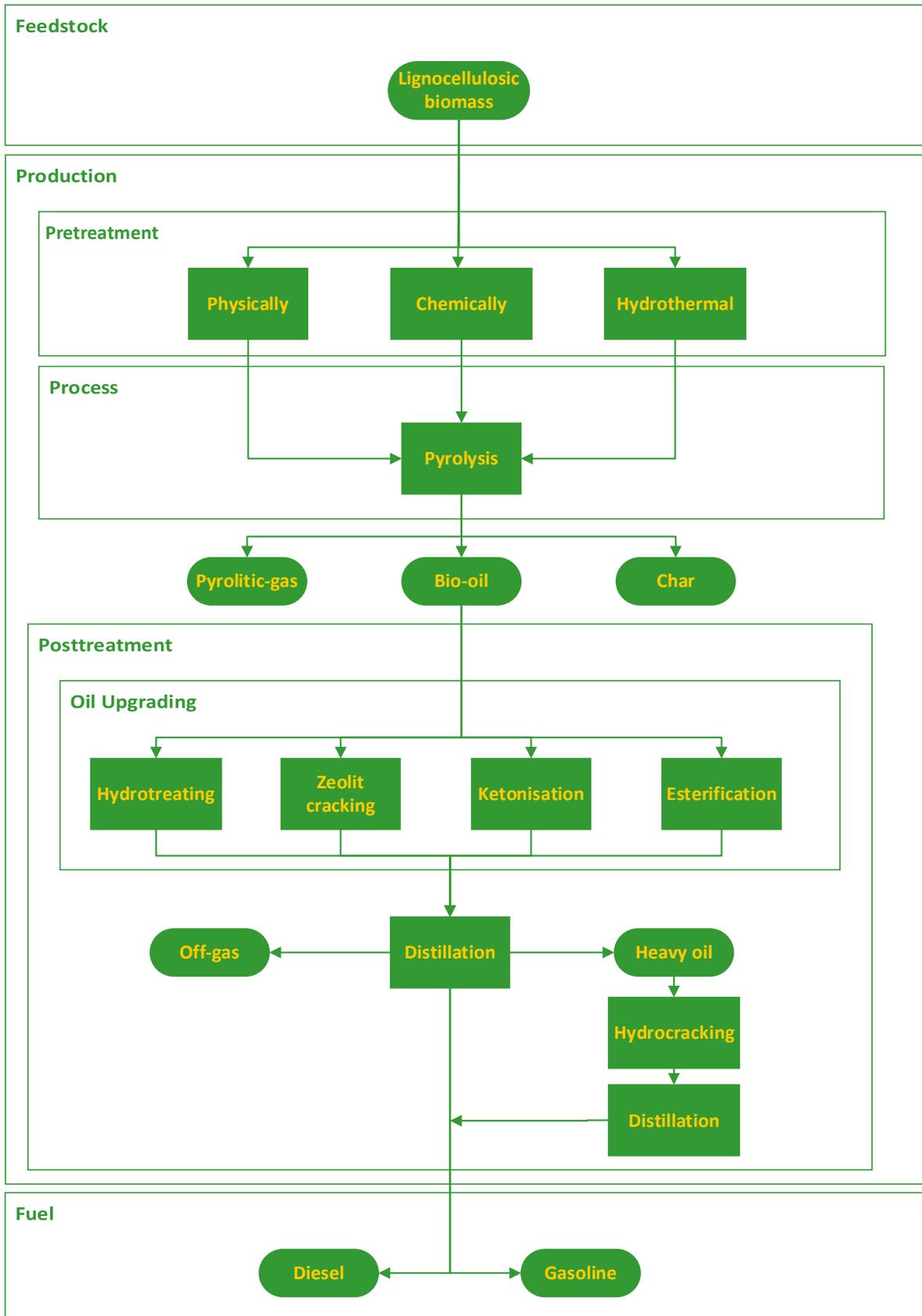


Figure 6-9: Reaction scheme of a possible pathway for pyrolysis-diesel/gasoline.

### 6.3.4.5 Hydrothermal Liquefaction

Another form of thermal decomposition of biomass feedstock can be hydrothermal liquefaction (HTL). This conversion technology is still in the stage of development and is therefore not explained in detail. The first plant that uses hydrothermal liquefaction technology has begun construction in Teesside, UK, and will be able to operate in 2022 [39]. This commercial-scale plant is designed to use plastic as feedstock and produce crude oil, which can be separated via distillation. Other feedstocks are lignocellulosic materials such as wood, straw seeds, leaves, as well as animal manures and organic fractions of municipal solid. HTL utilizes a combination of supercritical water chemistry in presence of a homogenous catalyst. At 373 °C and 220 bars water becomes supercritical [40]. In this state, it is not possible to distinguish between liquid or gaseous phase from water. Both phases are coexisting. In the pretreatment, the feedstock material gets crushed and diluted with water and catalysis mainly  $K_2CO_3$  or KOH. The solution is heated up to the critical stage of water. The reaction chemistry of hydrothermal liquefaction is complex and a lot of chemical reactions proceed depending on the operating condition. In addition, gasification can happen via a radical reaction in the range of 450 – 600 °C at a pressure of 50 – 250 bar. In HTL radical reactions are not favored due to the formation of coke. The reaction scheme in HTL is the ionic origin. The feedstock is depolymerized and oxygenated to crude oil and separated through distillation in different fractions. [41]

### 6.3.5 Synthetic Fuels

Synthetic fuels are almost exclusively produced from syngas as a precursor. Syngas is a gas mixture which consists primarily of carbon monoxide, hydrogen, and carbon dioxide. It can be produced from a variety of carbonaceous feedstocks and be used as a fuel itself, although its energy density is approximately half that of natural gas [42, 43, 44]. Therefore, it is often used as intermediate in synthetic processes producing hydrogen or hydrocarbon energy carriers such as synthetic natural gas (SNG), methanol, dimethyl ether, or FT fuels [45]. Among other factors, the molar ratio of  $H_2/CO$  in the synthesis gas mainly dependent on the type of feedstock. The gasification of coal, for instance, only yields a low  $H_2/CO$  ratio of  $\approx 1$ , whereas steam reforming of natural gas yields a higher  $H_2/CO$  ratio of  $\approx 3$  [46]. Depending on the requirements of the individual downstream application of the syngas, this ratio has to be adjusted either through an additional water-gas shift reaction or through the introduction of suitable catalysts in the gasification process. Today, syngas is mostly produced from fossil sources such as coal (mainly in China or South Africa) or natural gas (mainly in Europe or the United States). The technologies for syngas production from fossil sources are well established for decades and were abundantly discussed in literature (e.g., [44, 47, 48, 49, 50, 51, 52, 53]), and will not be discussed in the following. The following section first gives an overview over the syngas production from biomass gasification for SynBio fuels as well as the production of syngas via water electrolysis and CC technologies for SynNoBio fuels. Thereafter, a description of the possible synthesis routes for synthetic fuels is presented. A more detailed description of the syngas production processes and the FPPWs can be found in [54].

An interesting and heavily researched option for PtL pathways that is worth mentioning but not discussed here in detail is the direct co-electrolysis of  $CO_2$  and  $H_2O$ . This technology uses SOEL cells to produce syngas [55]. In contrast to the production of pure hydrogen via water electrolysis and the subsequent reduction of  $CO_2$  to CO via the reverse water-gas shift reaction (rWGSR) to produce syngas, this one-step process combines the reduction of  $CO_2$  and  $H_2O$  in one electrolyzer unit [43].

#### 6.3.5.1 Biomass Gasification for SynBio Fuels

The gasification process of biomass can utilize a wide variety of feedstocks, but the preferred types are lignocellulose and waste materials as they are no food competition or LUC concerns. Additionally, this

process makes use of the lignin content of biomass, which is usually difficult to break down using other bio-based fuel pathways-[42, 44, 46]. Prior to the main gasification process pre-treatment of the feedstock is necessary to homogenize the feedstock for an efficient gasification [56]. The pre-treatment involves processes such as drying, pulverization, and pelletization.

The gasification of biomass at temperatures of 750-950 °C requires a gasification agent, which is usually air, oxygen, or steam. The heat required for the gasification is partly provided by oxidation reactions, but the reaction is over all endothermic. However, the waste heat obtained from downstream synthesis processes can satisfy the heat demand via waste heat integration. The reactors used for biomass gasification are either fixed bed gasifiers, fluidized bed gasifiers, or entrained flow gasifiers. Fixed bed gasifier configurations can be classified in updraft and downdraft gasifiers and are used mainly in small scale plants. In larger scale plants, fluidized bed gasifiers are often the reactor of choice because of the easy scale-up. Entrained flow gasification technology has applications in large scale plants and has yet limited use for biomass gasification, as this process requires very fine powdered fuel particles < 1 mm which necessitates elaborate and expansive pre-treatment steps for the biomass fuel. Although there is not one dominant design, downdraft fixed bed gasifiers and fluidized gasifiers are the most popular configurations for biomass gasification. The biomass-derived syngas can be used as feedstock to produce a variety of fuels, both liquid such as methanol, ethanol, DME, and FT fuels, but also gaseous, such as hydrogen or SNG.

### Raw Syngas from Biomass Gasification

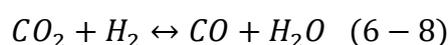
Several different contaminants can be found in biomass-derived syngas with their constitution and concentration depending on the type of feedstock and gasifier technology used. The main impurities are particulate matter, tar, sulfur and nitrogen compounds, alkali compounds, and chlorine [57]. Particulate matter found in raw syngas range in size from over 100 µm to less than 1 µm and their composition varies depending on feedstock and process. Tars have a very complex chemical nature and consist of hundreds or even thousand different condensable organic compounds like oxygenates, heavier deoxygenated hydrocarbons, or polycyclic aromatic hydrocarbons (PAHs). Hydrogen sulfide (H<sub>2</sub>S) and carbonyl sulfide (COS) are the main sulfur contaminants in raw syngas. Their concentrations mainly depend on the type of biomass feedstock, but it is worth mentioning that biomass generally has significantly less sulfur than coal leading to very low sulfur contents biomass-derived syngas compared to syngas made from solid fossil fuels. From proteins and heterocyclic aromatic compounds in biomass originate nitrogen contaminants, mostly ammonia (NH<sub>3</sub>), but also hydrogen cyanide (HCN). The content of alkali and alkaline earth metals in biomass is usually greater than it is in coal. Chloride salts of alkali metals are the main source of chlorine in biomass.

### Purification of Raw Syngas from Biomass

Purification of the raw syngas is necessary to either avoid minor problems such as process inefficiencies due to corrosion as well as catastrophic failures like permanent deactivation of the catalyst material in the downstream synthesis processes. Among the technologies used for syngas purification are “primary” or “in-situ” methods which attempt to minimize contaminant formation in the gasifier and “secondary” methods for cleaning the raw syngas downstream of the gasifier. The methods can be classified according to the syngas temperature during purification. Hot gas clean-up removes contaminants at temperatures 400 °C to up to 1300 °C. At the elevated temperatures tars are cracked thermally or catalytically, sulfur compounds are adsorbed on solid adsorbents. Ammonia is oxidized to N<sub>2</sub> by selective catalytic oxidation. Cold gas clean-up is referred to processes carried out below 100 °C and uses liquid adsorbents to remove contaminants. Warm gas clean-up covers the intervening temperature range and operates with cyclones, filters, and oil as scrubbing medium.

### 6.3.5.2 Syngas Production for SynNoBio Fuels

The pathways using coal, natural gas, or biomass all require extensive downstream clean-up operations as the feedstocks are contaminated with sulfur, nitrogen, alkali metals, and chlorine that form harmful compounds during syngas production which can be found in the raw syngas, along with tars and particulate matter [42, 43]. Therefore, the utilization of pure H<sub>2</sub> and CO<sub>2</sub> derived from water electrolysis and CC methods, respectively, is an interesting pathway for syngas production for PtL pathways. While in steam reforming and gasification applications the carbon in the feedstock is oxidized to carbon monoxide, the use of carbon dioxide as carbon source requires a reduction reaction. This reduction of the oxidation state of carbon from C<sup>(4+)</sup>O<sub>2</sub> to C<sup>(2+)</sup>O is carried out via the rWGSR, which is illustrated in formular 6 – 8. [43].



In addition to the avoidance of complex clean-up processes of the produced syngas, the use of carbon dioxide and water as starting materials also brings the advantage of adjustable H<sub>2</sub>/CO ratios. Syngas from coal gasification only yields a low H<sub>2</sub>/CO ratio of about 1 and necessitates an increase of the hydrogen content to be used for catalytic processes. This increase is accomplished by an additional water-gas shift reaction that in fact raises the hydrogen content, but at the expense of a part of the carbon is being lost as CO<sub>2</sub> as exhaust. In PtL applications the rWGSR reduces CO<sub>2</sub> to CO at the expense of decreasing the hydrogen content through the formation of water. But in contrast of being lost, the produced water can be cycled back to the electrolysis system [43]. A defined syngas composition is required for all downstream catalytic processes. At a molar H<sub>2</sub>/CO ratio of 3 methanation produces methane or SNG, FT synthesis to produce hydrocarbon fuels as well as methanol synthesis both require a H<sub>2</sub>/CO ratio of 2 [45].

#### 6.3.5.2.1 Water Electrolysis

Hydrogen as a starting material is supplied by the electrolysis of water. The technologies for electrochemical water splitting all follow the same basic principle. A direct current is applied to two electrodes to produce hydrogen at the cathode and oxygen at the anode from a water or water vapor feed. The demands on the purity of water differ between the various electrolyzer types, but usually ASTM Type II (1.0 Ω·cm or 1.0 μS·cm<sup>-1</sup>) or even ASTM Type I (18.2 Ω·cm or 0.055 μS·cm<sup>-1</sup>) is required since impurities can deposit on the electrode surfaces and in the membrane of electrolysis cells [58]. Possible water sources are manifold, the most promising for large scale electrolysis hydrogen production are groundwater, tap water, wastewater, seawater, surface water, and rainwater. The processes generally used for water purification are fine screening, coagulation-flocculation and filtration, ultrafiltration, and reverse osmosis. Fine screening is used to removes solid particles using screens with typical opening sizes of 1.5-6 mm<sup>2</sup>. Coagulation-flocculation and filtration uses coagulating agents to remove particles and suspended solids. As an alternative to remove small particles ultrafiltration using membranes. Small particles, but also dissolved solids or inorganic ions, as well as organic and biological species can be removed with reverse osmosis. In this process using a semi-permeable membrane pressure is applied to overcome the osmotic pressure and force water through the membrane.

The minimum voltage required to split liquid water into hydrogen and oxygen at is 1.23 V. The thermo-neutral voltage of 1.5 V enables the electrolysis of liquid water at a constant temperature without the requirement of further heating. If above 100 °C water vapor is provided to the electrolysis cell the thermo-neutral voltage drops to 1.3 V. Accordingly, there are three zones of operation for electro-chemical water splitting as illustrated in Figure 6-10. Applied cell potentials above the thermo-neutral voltage lead to the production of heat (exothermic operation) and require cooling of the electrolysis cell. If operated below

the thermo-neutral voltage but above the equilibrium voltage (endothermic operation) the cell cools down and requires heating. The operation of a water electrolysis cell below the equilibrium voltage is not possible [59, 60].

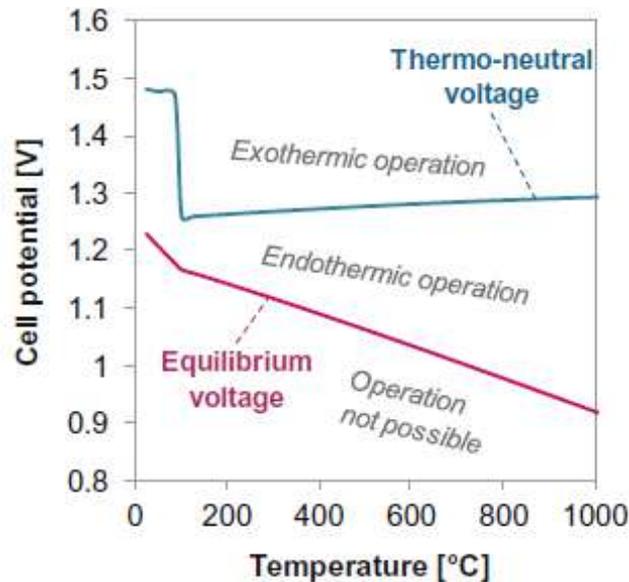


Figure 6-10: Temperature-dependence of the equilibrium voltage and thermo-neutral voltage in electrolysis cells [60].

The three types of water electrolyzer currently available are alkaline electrolysis (AEL), proton exchange membrane electrolysis (PEMEL), and solid oxide electrolysis (SOEL) as depicted in Figure 6-11. The first two are classified as low temperature electrolysis processes using liquid water, the latter is a high temperature application using water vapor as feed. AEL and PEMEL are operated above the thermo-neutral voltage due to overpotentials and internal losses in the cell at operation voltages in the range of 2 V. SOEL cells are operated at constant temperatures and thermo-neutral voltages [59, 60]. The efficiency of an electrolysis cell is indicated by the operational voltage. Higher voltages than the thermo-neutral voltage mean a higher power demand for hydrogen production. A more detailed view on the efficiency of the electrolyzer types is presented in section 7.3 of this report.

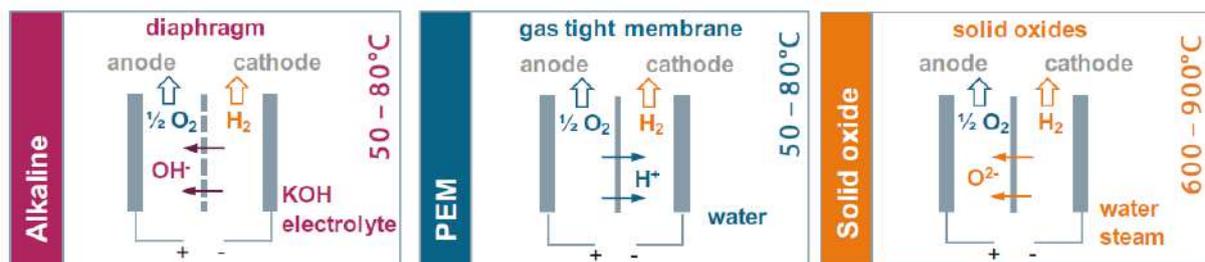


Figure 6-11: Basic types of water electrolysis technologies [60].

### Alkaline Electrolysis (AEL)

The alkaline electrolysis of water for hydrogen generation is a very mature technology (TRL = 9) that has been used for over a century commercially and currently still is the standard process for electrochemical hydrogen production [59, 60, 61]. Large scale industrial electrolysis plants use a power input of about 130 MW to produce  $> 10^4$  Nm<sup>3</sup> hydrogen per hour [60]. In AEL applications the electrodes are immersed in an aqueous solution of potassium hydroxide (KOH) or sodium hydroxide (NaOH) with concentrations of 25-30 wt%. This highly caustic solution serves as electrolyte responsible for carrying the electrical charge through the liquid phase via OH<sup>-</sup> ions. In the highly alkaline environment various nonnoble metals are stable and can be used as electrode material and catalysts. The electrodes are usually made of low-carbon



steel, the anode is mostly plated with catalytically active Ni. The electrodes are separated by a diaphragm made of PEEK and titanium oxide to prevent the product gases from mixing and placed as closely as possible to each other to minimize the ohmic resistance of the electrolyte [62]. To remove the product gases and heat the electrolyte is circulated either by pumps or by natural convection. After drying, hydrogen qualities of 99.5-99.9 % can be achieved which can be increased to 99.999 % by catalytic purification. The drawbacks of AEL are low current densities between  $0.2 \text{ A}\cdot\text{cm}^{-2}$  and  $0.5 \text{ A}\cdot\text{cm}^{-2}$  and low dynamic behavior under part load conditions. The large volume of highly caustic electrolyte is also a safety issue [59, 63].

### Proton Exchange Membrane Electrolysis (PEMEL)

Proton exchange membrane electrolysis sometimes also referred to polymer electrolyte membrane electrolysis was introduced in the 1960s and are commercially available only for small and medium scale applications today (TRL = 7-8) [59, 60, 61, 63]. The typical energy input for PEMEL is around 1 MW. Compared to AEL this technology offers much higher current densities of  $1.0\text{-}2.0 \text{ A}\cdot\text{cm}^{-2}$ , the possibility of a more compact design and higher hydrogen purity  $> 99.99 \%$  [59]. The operational flexibility and the possibility of fast start up and highly dynamic operation is an important advantage of PEMEL over AEL, especially with fluctuating loads from renewable energy sources like solar and wind power. For example, a polymer membrane electrolyzer can be ramped up from stand-by to full load in under 10 s and be operated from 0-100 % nominal load, even short-time operation of 150 % is possible [59].

The core of the PEMEL technology is a thin, robust, and gastight polymeric electrolyte membrane that separates the electrodes and facilitate the transport of  $\text{H}^+$  charge carriers. This ionomer has a perfluorocarbon backbone with functional sulfonic acid groups, that are responsible for the proton conductivity of the membrane. Reducing the thickness also reduces the ohmic resistance of the solid electrolyte and leads to improved efficiencies. However, thin membranes are prone to damage through mechanical stress due to pressure fluctuations which limits the lifetime of the electrolysis cell [59, 63]. The electrodes are directly mounted on the membrane, forming a membrane electrode assembly [62]. The highly acidic environment of the membrane necessitates the use of expensive noble metals as catalysts. The oxygen generation on the anode is catalyzed by noble metal oxides, such as  $\text{RuO}_2$  or  $\text{IrO}_2$ , the cathode comprises of porous graphite coated with platinum. The relatively high production cost of  $\text{H}_2$  compared to AEL due to high cost of precious metals used as catalysts and the application of only small-scale production plants is the major drawback of PEMEL technology. But since PEMEL is the preferred technology to utilize the intermittent supply of renewable energy from wind and solar power great efforts are made in up-scaling of electrolysis plants and research for cheaper electrocatalysts [59].

### Solid Oxide Electrolysis (SOEL)

Compared to AEL and PEMEL, SOEL is a novel technology developed in the 1980s (TRL = 6) [59, 60]. The technology is still in the demonstration stage but the thermodynamical and electrochemical advantages as well as potential of using relatively low-priced materials make it the center of many research projects [60]. The largest SOEL module to date was manufactured by German company sunfire for the EU pilot project MultiPLHY with the goal of producing synthetic fuels from hydrogen and renewable energy [64]. This project aims to build the world's first multi-megawatt SOEL plant in Rotterdam with a total capacity of 2.4 MW. The largest single SOEL module comprises of 60 stacks with 1,800 electrolysis cells producing  $63 \text{ Nm}^3\cdot\text{h}^{-1}$  with a specified efficiency of over 80 %.

The high efficiencies of SOEL applications are the result of the high operating temperatures of  $700\text{-}900 \text{ }^\circ\text{C}$  as the reaction kinetics are improved and the thermo-neutral voltage steam electrolysis is lower (1.3 V) than that of liquid water electrolysis (1.5 V) [59, 60, 65, 66]. This leads to a considerable drop of the total energy demand above  $100 \text{ }^\circ\text{C}$  under atmospheric pressure. Therefore, SOEC operated at high

temperatures require less electricity for water electrolysis and can lead to reduced cost for hydrogen production. The large amount of heat required for steam generation and the high final temperatures can be partly recuperated from the product gas streams, although additional heating is necessary. This can either be realized through electrical heating or integration of waste heat from subsequent exothermal synthetic processes, such as methanol or FT synthesis [59, 65].

A SOEC stack comprises of planar electrolysis cells with a typical thickness of 200-300  $\mu\text{m}$  electrically connected in series. The solid electrolyte has to be highly conductive for  $\text{O}^{2-}$  ions and is usually made from yttrium-stabilized zirconia (YSZ), a zirconium oxide ceramic material doped with 8 mol% yttrium oxide. The reduction of steam to hydrogen happens at the cathode. Therefore, steam as well as recycled hydrogen to maintain reducing conditions is fed to this electrode made of a ceramic-metal compound composed of YSZ and nickel. Nickel as a non-precious metal acts as a catalyst for the reduction reaction [66]. The product at the cathode is a mixture of hydrogen and steam which is separated by cooling and condensing the water. The anode is usually made from materials with a perovskite structure ( $\text{ABO}_3$ ), such as  $\text{SrCoO}_3$ . The major drawback of SOEL are challenges regarding material stability under the high operating temperatures. SOEC cells are currently operated below the thermo-neutral voltage and at current densities below  $1 \text{ A}\cdot\text{cm}^{-2}$  to mitigate degradation of both the cathode and the anode. The high temperatures also lead to long start-up times and hinders flexible operation [59].

### Comparison of AEL, PEMEL and SOEL

Both AEL and PEMEL are operated in the same temperature range below the boiling point of water, whereas SOEC is operated at elevated temperatures of up to  $900 \text{ }^\circ\text{C}$ . The main process parameters of AEL, PEMEL, and SOEL are presented in **Fehler! Verweisquelle konnte nicht gefunden werden.** Table 6-7 [59]. Since hydrogen is usually stored and utilized at high pressures the pressurized operation of electrolysis systems can be beneficial. The reduction of initial investment costs and maintenance through the elimination of a downstream compressor, however, is traded against slightly higher operation voltages, increased degradation, and cross permeation of the reactant gases leading to safety issues from flammable gas mixtures. Therefore, AEL and PEMEL are usually operated at moderate pressures of 30-50 bar. The pressurized operation of SOEC stacks is under investigation and commercial modules (e.g., HYLINK SOEC from sunfire) deliver hydrogen at ambient pressure. The efficiencies in Table 6-7 are expressed in relation to the LHV of hydrogen. Commercial AEL electrolysis stacks show rated efficiencies of 63-71 %<sub>LHV</sub> and stack energy consumptions of  $4.2\text{-}4.8 \text{ kWh}\cdot\text{Nm}^{-3}$ . PEMEL stacks offer efficiencies ( $\eta_{\text{LHV}} = 60\text{-}68 \%$ ) and energy consumptions ( $4.4\text{-}5.0 \text{ kWh}\cdot\text{Nm}^{-3}$ ) in the same range. However, much higher current densities of up to  $2.0 \text{ A}\cdot\text{cm}^{-2}$  can be reached with PEMEL compared to  $0.45 \text{ A}\cdot\text{cm}^{-2}$  with AEL, resulting in higher hydrogen yields per cell area. Most SOEL cells are operated at up to  $1.0 \text{ A}\cdot\text{cm}^{-2}$  with close to 100 % efficiencies based on LHV when operated at thermoneutral voltage. Using heat integration system efficiencies of up to 81 %<sub>LHV</sub> have been reported. Part load operation capability is an important parameter for hydrogen production technologies based on renewable energies due to the load fluctuations of solar and wind energy production. AEL minimum load is limited to 20 % due to diffusion of hydrogen through the electrolyte to the oxygen electrode. This leads to a highly flammable hydrogen-oxygen mixture at low loads. The resistance of polymer membranes against gas permeation allows for a load range of 0-100 % nominal load. SOEL cells can even be operated in reversible mode as fuel cells leading to an operational range of  $-100$  to  $+100 \%$ .

Table 6-7: Parameters of water electrolysis technologies [59].

Parameters	AEL	PEMEL	SOEL
Cell temperature [°C]	60-90	50-80	700-900
Pressure [bar]	10-30	20-50	1
Current density [ $A \cdot cm^{-2}$ ]	0.25-0.45	1.0-2.0	0.3-1.0
Load flexibility [% of nominal load]	20-100	0-100	-100/+100
Cold start-up time	1-2h	5-10 min	Hours
Warm start-up time	1-5 min	< 10 s	15min
Nominal stack efficiency (LHV)	63-71 %	60-68 %	100 %
Nominal stack energy consumption [ $kWh \cdot Nm^{-3}$ ]	4.2-4.8	4.4-5.0	3
Nominal system efficiency (LHV)	51-60 %	46-60 %	76-81 %
Nominal system energy consumption [ $kWh \cdot Nm^{-3}$ ]	5.0-5.9	5.0-6.5	3.7-3.9
H <sub>2</sub> production per stack [ $Nm^3 \cdot h^{-1}$ ]	1400	400	< 10
Cell area [ $m^2$ ]	< 3.6	< 0.13	< 0.06
TRL	9	7-8	6

### 6.3.5.2.2 Carbon Capture

The carbon feedstock for PtL derived fuels is CO<sub>2</sub>, either captured before the combustion of a fuel or from concentrated point sources after the combustion process, or directly from the air via DAC [45]. Industrial point sources providing relatively pure CO<sub>2</sub> streams are bioethanol production via fermentation and ammonia synthesis plants, where the production of 1 ton of ammonia yields 1.8 tons of CO<sub>2</sub> [67]. Biogas from the anaerobic digestion of organic waste such as sewage sludge, food waste, animal manure or crop residues is composed of roughly 55-75 % CH<sub>4</sub> and 25-45 % CO<sub>2</sub>. Other industries generate off gas streams with CO<sub>2</sub> concentrations of up to 30 %, such as cement plants and steel mills. The flue gases from power plants have rather low CO<sub>2</sub> contents in the range of 3-12 %. Capturing CO<sub>2</sub> from these industrial point sources may seem favorable due to the high CO<sub>2</sub> content of the off-gas streams. However, concentrated point sources may not be available for PtL fuel production if they are not in close proximity to the fuel production plant. Additionally, in a decarbonized future point sources will become scarce. An inexhaustible source of CO<sub>2</sub> is air. However, compared to point sources the CO<sub>2</sub> concentration in the ambient air is very low, necessitating great efforts for CO<sub>2</sub> capturing. Table 6-8 gives an overview over some important CO<sub>2</sub> sources and their CO<sub>2</sub> concentrations.

Table 6-8: Concentration of CO<sub>2</sub> in various point source off-gas streams and in the atmosphere [68, 67, 69, 70, 71].

Source	CO <sub>2</sub> concentration [vol%]	Common impurities
Fermentation of biomass	99	EtOH, MeOH, H <sub>2</sub> S, H <sub>2</sub> O, C <sub>2</sub> H <sub>6</sub> S
Ammonia synthesis	> 95	NH <sub>3</sub> , H <sub>2</sub> , CO, H <sub>2</sub> O
Anaerobic digestion of biomass	25-45	CH <sub>4</sub> , H <sub>2</sub> S, N <sub>2</sub> , H <sub>2</sub> O
Cement plants	15-33	O <sub>2</sub> , NO <sub>x</sub> , SO <sub>2</sub>
Steel plants	14-27	N <sub>2</sub> , CO, H <sub>2</sub> , H <sub>2</sub> S, Mn, Pb, Zn
Coal-fired flue gas	10-12	NO <sub>x</sub> , SO <sub>x</sub> , CO, O <sub>2</sub> , N <sub>2</sub> , Hg, As, Se
Gas-fired flue gas	3-6	NO <sub>x</sub> , SO <sub>x</sub> , CO, O <sub>2</sub> , N <sub>2</sub> , Hg, As, Se
Atmospheric CO <sub>2</sub>	0.0419	N <sub>2</sub> , O <sub>2</sub>

The technologies for carbon capturing from point sources can be classified in either chemical or physical absorption processes, adsorption processes, membrane separations, carbonate looping, and oxyfuel combustion [72, 73].

## Absorption Technologies

Chemical absorption processes are based on the principle of using solvents that form chemical bonds with CO<sub>2</sub> in chemical reactions. This process has been employed in large-scale applications since the 1930s in the form of amine scrubbing using aqueous solutions amines (TRL = 9) [72, 74]. Amins react with CO<sub>2</sub> in an absorber vessel, where the gas stream bubbles through the solvent. The sorbent is subsequently regenerated in a stripping column to desorb the captured CO<sub>2</sub>. Due to a limited loading capacity of the solvent and the high energy requirement for the sorbent regeneration other chemical systems are also used, such as aqueous ammonia or potassium carbonate.

In contrast to chemical absorption, physical absorption processes are not based on chemical reactions but on the principle that CO<sub>2</sub> dissolves in suitable solvents. The capacity for CC of the solvents is best at low temperatures, so the gas stream needs to be cooled before entering the absorber vessel. Physical absorption has been realized for example in the Rectisol process using methanol and the Selexol process using dimethyl ethers of polyethylene glycol (both TRL = 9). Although methanol seems favorable due to its low cost, the need for cooling to absorber for achieving a satisfying CO<sub>2</sub> capacity is energy intensive. Polyethylene ethers on the other hand are very stable, however, they require high CO<sub>2</sub> concentrations in the gas stream and are rather cost intensive [73]. The solvents in physical absorption processes are generally regenerated by reducing the pressure. Therefore, no thermal energy is required for the desorption of CO<sub>2</sub> from the solvent as it is in chemical absorption processes. However, electrical energy to operate the pressure swing is necessary [62].

## Adsorption Technologies

While absorption processes facilitate the whole volume of the solvent to capture CO<sub>2</sub>, adsorption processes only happen on the surface of a solid (TRL = 6-8). Here, CO<sub>2</sub> adheres to the surface of a sorbent and is so separated from the feed gas stream. Usually, the sorbent is placed in a column and the CO<sub>2</sub> gas feed is led through the sorbent bed. When the sorbents surface is saturated with CO<sub>2</sub> different strategies can be pursued to release the captured carbon and regenerate the sorbent bed to recover the concentrated CO<sub>2</sub> [72]. In a process called pressure swing adsorption (PSA), the pressure in the column is reduced to force the CO<sub>2</sub> molecules back in the gas phase. This is particularly attractive for high pressure feed gases. If the pressure of the gas feed is close to atmospheric pressure, vacuum swing adsorption (VSA) processes can be used. In this variety of PSA, the pressure in the column is decreased to a partial vacuum. Temperature swing adsorption (TSA) is carried out by elevating the temperature of the sorbent to a point, where the surface bonds of CO<sub>2</sub> are broken. Generally, TSA is better suited for chemical adsorption where the interaction of CO<sub>2</sub> with the sorbent surface includes chemical bonds, whereas PSA is used for physical adsorption where the interactions are based on van der Waals forces [72].

## Membrane Technologies

Gas mixtures can also be separated using membranes as semipermeable barriers (TRL = 7-8). At high pressures, the CO<sub>2</sub> bearing gas mixture is led onto the membrane which only allows CO<sub>2</sub> to pass through. On the permeate side, a lower pressure is applied to help the flux through the membrane. The variety of membrane materials used in CC applications vary from metals, silica, and zeolites with excellent selectivity for hydrogen in precombustion applications, to cellulose acetate, polyamides, polysulfones, and polycarbonates for the separation of CO<sub>2</sub> from N<sub>2</sub> in post-combustion carbon capturing [75].

## Calcium Looping

Calcium looping utilizes the lime carbonation/calcination circle (TRL = 7). In this circle, calcium oxide is used as sorbent for CO<sub>2</sub> to form calcium carbonate. At temperatures around 650 °C and at atmospheric pressure CO<sub>2</sub> reacts with CaO in a reaction vessel (carbonator) and is so separated from the gas stream.

The formed  $\text{CaCO}_3$  is then transferred in a second reaction vessel called calcinator where it is regenerated to  $\text{CaO}$  at temperatures around  $900\text{ }^\circ\text{C}$  for further use in the carbonator. The pure  $\text{CO}_2$  released in the calcinator can be pressurized and stored for further use [69]. Since carbonation is an exothermic reaction, the generated reaction heat can be utilized for steam and electricity generation, improving the overall process efficiency [69, 74].

### Oxyfuel Process

The oxyfuel process is also classified as a post combustion technology (TRL = 6-8). But in contrast to combust fuels with ambient air, pure oxygen from an air separation unit is used. This leads to a post combustion gas stream of almost pure  $\text{CO}_2$  and  $\text{H}_2\text{O}$  without  $\text{NO}_x$  and  $\text{SO}_x$  components. The water can easily be condensed, and no further gas separation measures are necessary. However, the generation of pure oxygen induces an energy penalty which leads to a reduction in overall plant efficiency [74, 76].

In direct air capture application  $\text{CO}_2$  from the atmosphere is captured. In mid of 2021, the atmospheric  $\text{CO}_2$  content measured at NAOO's Mauna Loa Atmospheric Baseline Observatory was approximately 419 ppm [71]. In contrast to point sources, the DAC approach is more energy intensive due to the extremely low concentration of  $\text{CO}_2$  in the ambient air compared to flue gas streams. However, DAC plants can be operated virtually anywhere in the world and can therefore facilitate the on-site production of PtL fuels at locations with high wind or solar energy production potential [62]. Currently, only a handful of companies are active in the field of DAC (Figure 6-12), differing in their technical approach to CC solutions from the air [77, 78]. The world's largest DAC facility is operated by Climeworks and started operation in September 2021 [79]. Located in Hellisheiði, Iceland, the plant powered by renewable geothermal energy removes  $4 \cdot 10^3$  tons of  $\text{CO}_2$  per year.

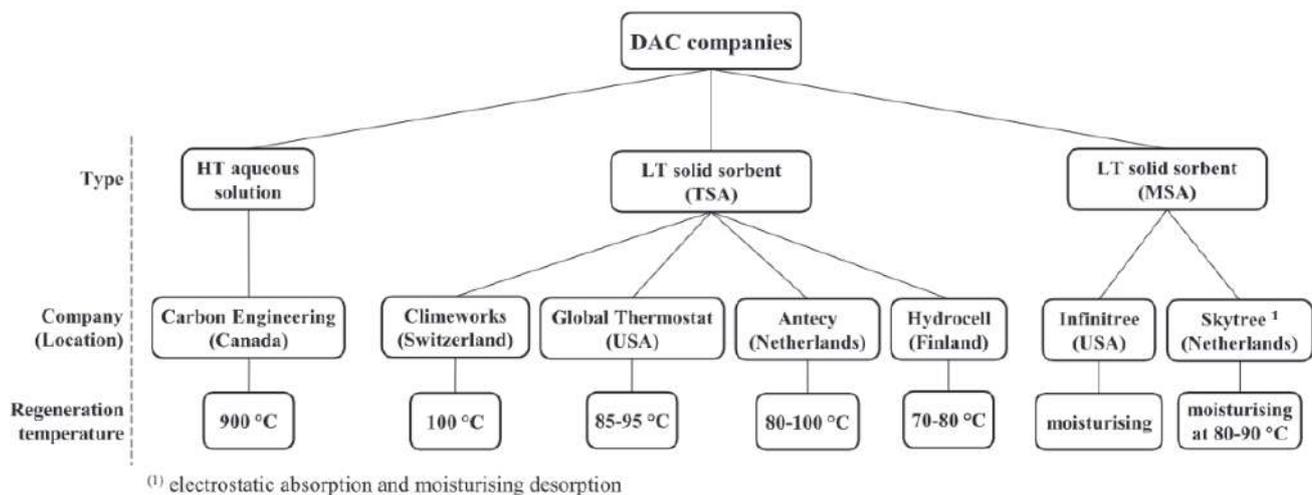


Figure 6-12: Companies providing DAC solutions; HT = high temperature; LT = low temperature; TSA = temperature swing adsorption; MSA = moisture swing adsorption [78].

### Low Temperature Solid Sorbent Technology

The low temperature solid sorbent technology is based on the principle that ambient air is being pushed through filters mounted in filter chambers by fans (Figure 6-13). The  $\text{CO}_2$  is retained by the filters and  $\text{CO}_2$  depleted air exits the filter chamber. At ambient temperatures  $\text{CO}_2$  chemically binds to the filter material by adsorbing to solid amine-based adsorbents [74]. Cellulose fiber filters supported by solid amines are used by Climeworks, Global Thermostat uses an amino-polymer [78]. Once the filter is saturated the filter chamber is isolated from the ambient air. The pressure in the chamber is reduced and the temperature is

increased to around 100 °C to release the captured CO<sub>2</sub> into a storage tank. After cooling, the process starts anew [77].

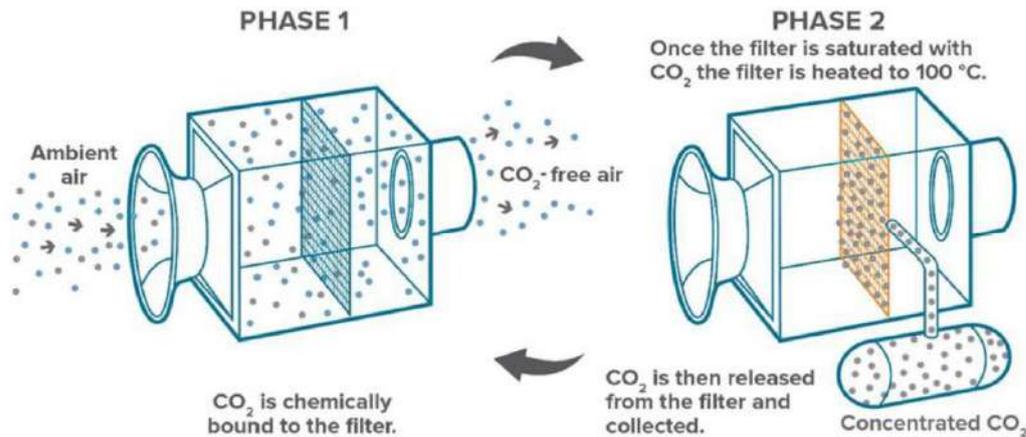


Figure 6-13: Schematic of Climeworks DAC process [77].

### High Temperature Solid Sorbent Technology

Carbon capturing by high temperature aqueous solutions is pursued by Carbon Engineering. Carbon engineering was established in 2009 in Squamish, Canada and is funded, among others, by Bill Gates [80]. The pilot plant operated in Squamish since 2015 captures 1 ton of CO<sub>2</sub> per day, and the company is planning to begin construction on the first large-scale commercial CO<sub>2</sub> capturing plant in Permian Basin, U.S. in 2022. This plant will be expected to capture one million tons of CO<sub>2</sub> per year once fully operational [81].

The technology is based in the principle illustrated in Figure 6-14 and comprises of two connected chemical loops [82]. In the first loop CO<sub>2</sub> from ambient air is captured by using fans to push the air through a sprayed aqueous solution of sodium hydroxide in the absorber called air contactor. CO<sub>2</sub> reacts with NaOH to form a solution of sodium carbonate at room temperature. CO<sub>2</sub> depleted air leaves the air contactor, and the carbonate solution is transported to the regeneration loop. In a causticizer, sodium carbonate is mixed with calcium hydroxide to yield solid calcium carbonate and regenerated sodium hydroxide. The energetic drawback of this technology is the next step in this cycle, where CO<sub>2</sub> is released from the solid CaCO<sub>3</sub> pellets by heating it up to around 900 °C in a calciner unit. The exit streams of the calciner are calcium oxide and a pure stream of CO<sub>2</sub> that can be pressurized and stored. The solid calcium oxide is mixed with water in the slaker unit to regenerate Ca(OH)<sub>2</sub> for the next cycle as seen in formular 6 - 9:



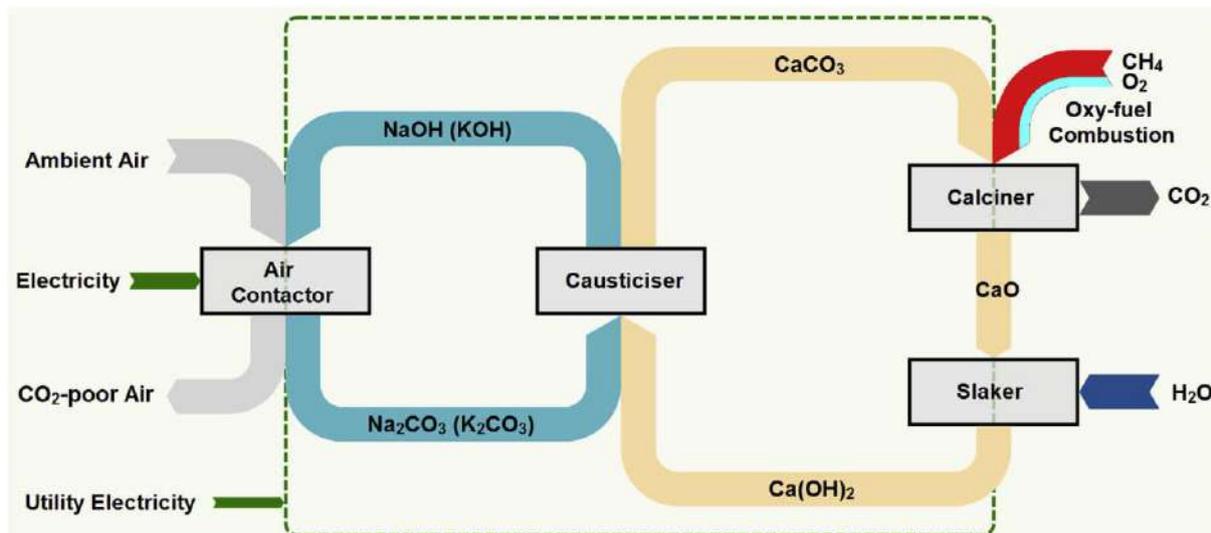


Figure 6-14: Process of DAC based on aqueous solution of sodium hydroxide or potassium hydroxide [78].

To provide the high-grade heat demand of the calciner reaction, the solution most discussed in literature is the oxy-fuel combustion of natural gas. However, powered by natural gas, this technology would release about 0.5 tons of CO<sub>2</sub> per captured ton of atmospheric CO<sub>2</sub> from fossil sources. The use of SNG could circumvent this issue, but at the cost of a huge increase of primary energy demand and production costs for SNG production. Thus, a fully electrified high temperature DAC (HT-DAC) process using electric heating are discussed as the most promising solution [78].

### 6.3.5.3 Fuel Synthesis

The two main pathways currently discussed for synthetic fuel production processes are the FT synthesis pathway and the methanol pathway [83]. The general scheme of the production processes is illustrated in Figure 6-15 and Figure 6-16.

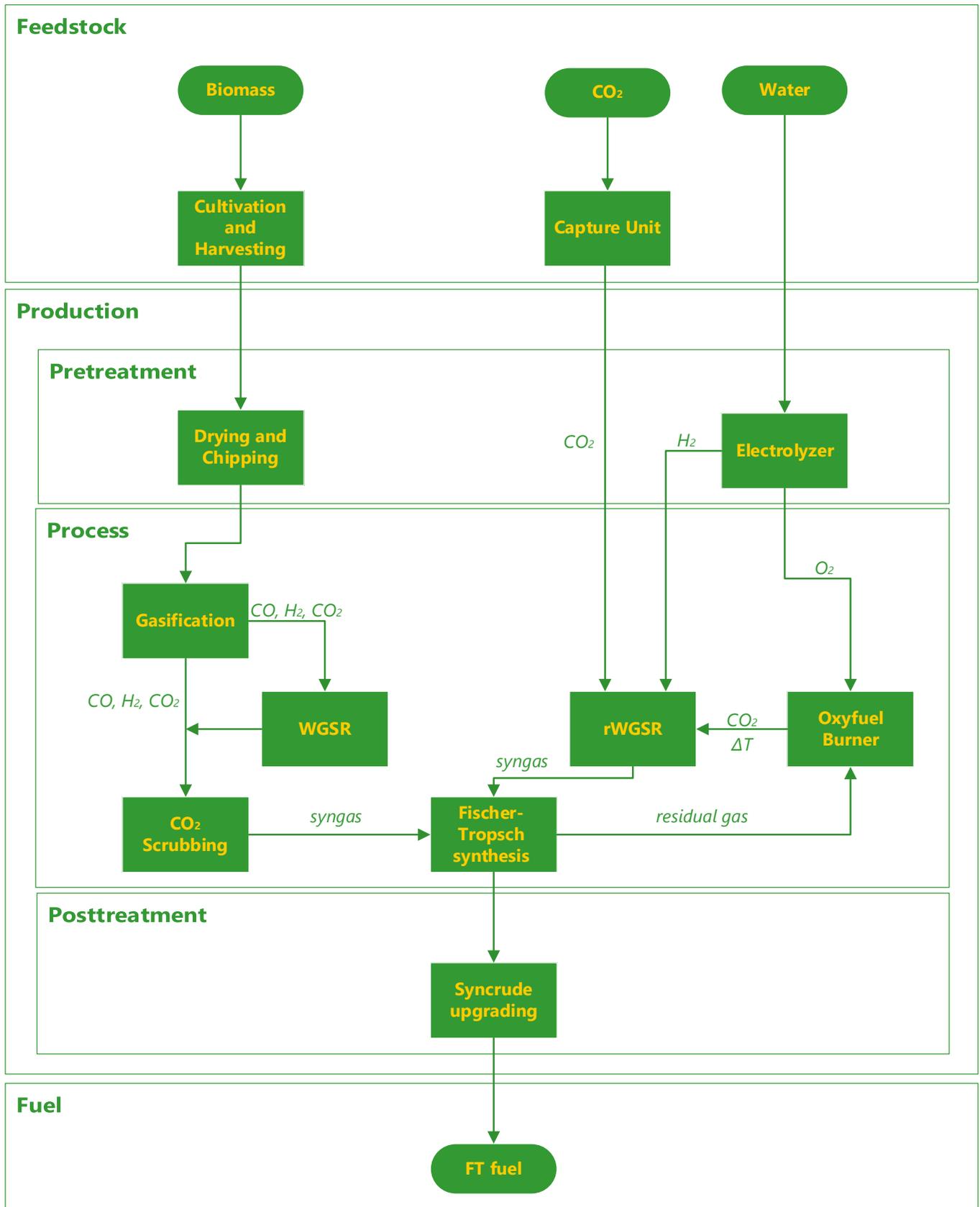


Figure 6-15: General scheme of BtL and PtL production pathways via FT synthesis.

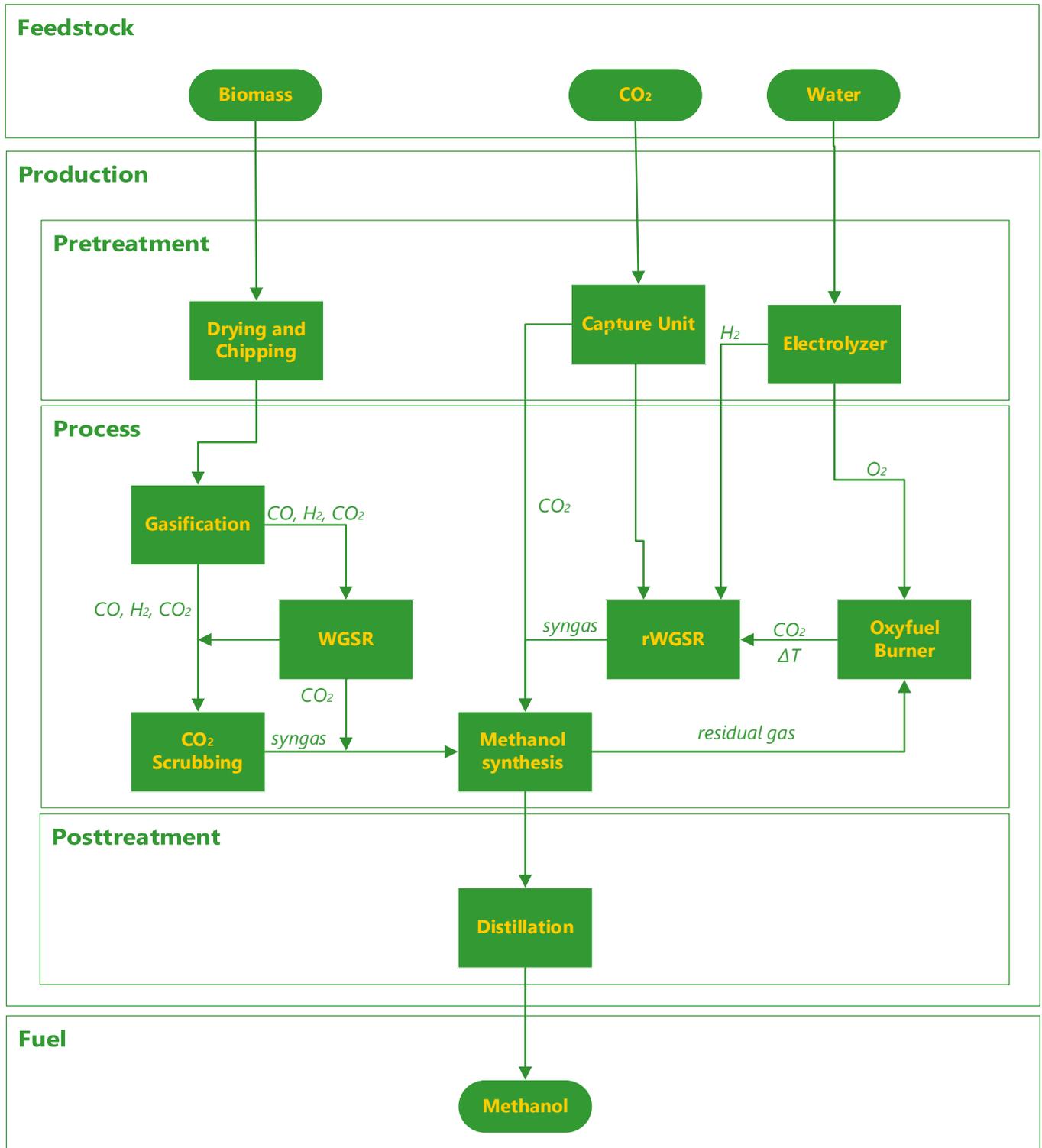
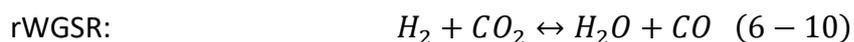


Figure 6-16: General scheme of BtL and PtL production pathways via methanol synthesis.

The FT synthesis allows for the production of high quality, almost sulfur-, nitrogen-, and aromatics-free transportation fuels from syngas [42, 45, 84, 85, 86]. Especially in FT diesel fuels the absence of sulfur, nitrogen, and aromatic compounds is beneficial due to improved exhaust emissions [85]. The produced FT fuels are very similar to CFFs and so compatible with the current vehicle fleet and refueling infrastructure [45, 83, 87].

Methanol can be used as blending material for conventional gasoline or directly as fuel in modified combustion engines [88]. It can serve as platform chemical for the production of the diesel additives DME and OME, which in turn can be used as diesel fuel substitutes. It also offers the possibility to produce synthetic gasoline via the methanol to gasoline (MtG) route [45, 89].

Both methods utilize syngas which either originates directly from biomass gasification in biomass to liquid (BtL) pathways or can be produced from captured CO<sub>2</sub> and hydrogen obtained from water electrolysis in PtL pathways. PtL syngas is produced via a rWGSR (formula 6 – 10):



In this equilibrium reaction hydrogen and CO<sub>2</sub> are converted to water and CO at temperatures around 1000 °C and pressures of up to 50 bar using iron carbide catalysts. The high temperature can be provided by an oxyfuel burner fed with unreacted off gas from the synthesis reactor and oxygen from the water electrolysis [62]. The rWGSR step to produce syngas for PtL processes is still heavily researched and least mature process of a PtL pathway (TRL = 6). Alternatively, PtL syngas can be obtained by the co-electrolysis of water and CO<sub>2</sub> [83].

To adjust the composition in the case of low H<sub>2</sub>/CO ratio syngas from biomass gasification, the aforementioned reaction is used in the opposite direction as water-gas shift reaction (WGSR). Here, steam is added to a partial stream of the syngas at temperatures of 220-260 °C to increase the H<sub>2</sub> content of the syngas and adjust it to the desired H<sub>2</sub>/CO ratio of two before entering the synthesis-reactor. Other than the rWGSR, this process step is mature technology with TRL = 9. However, this reaction causes a loss of carbon in the form of CO<sub>2</sub>, which is generally captured in a subsequent Selexol or Rectisol process [62]. Other than the FT synthesis, the methanol synthesis pathway requires low concentrations of CO<sub>2</sub> in the range of 3-10 vol% in the gas feed to the reactor. Therefore, not all carbon dioxide is removed from the syngas stream before entering the methanol synthesis reactor.

To avoid the unwanted production of CO<sub>2</sub> while adjusting the H<sub>2</sub>/CO ratio in the WGSR reactor in BtL pathways and improve the carbon efficiency of the overall process, BtL and PtL pathways can be combined to power and biomass to liquid (PBtL) processes. Here, the syngas produced by biomass gasification is adjusted to the desired H<sub>2</sub>/CO ratio by adding hydrogen obtained by a water electrolyzer unit. The hydrogen can be mixed directly with the biomass derived syngas or led to a rWGSR reactor. In the rWGSR the hydrogen is mixed with the syngas and CO<sub>2</sub> from an oxyfuel burner to yield syngas with the desired H<sub>2</sub>/CO ratio of two. The oxygen generated by the electrolyzer can be used either as a gasification agent in the biomass gasification step or in the oxyfuel burner providing the heat for a rWGSR reactor [62].

### 6.3.5.3.1 Fischer-Tropsch Synthesis

The FT synthesis (TRL = 9) to produce liquid hydrocarbons from syngas was developed in Germany in the 1920s by Franz Fischer and Hans Tropsch at the Karl-Wilhelm-Institut für Kohlenforschung in Mülheim an der Ruhr [90]. During World War In the 1970s where the government-backed company South Africa Synthetic Oil Limited (SASOL) was founded in South Africa to produce liquid fuels from coal derived syngas [91]. Currently, SASOL operates the largest coal to liquid (CtL) FT plant in the world in Secunda in South Africa. 45 million tons of coal are processed per year in its two production units SASOL II and SASOL III build in the 1980s, which were upgraded to the SASOL Advanced Synthol (SAS) process at the end of the 20<sup>th</sup> century [92]. The largest GtL facility in the world is operated by Qatar Petroleum and Shell since 2012 in Ras Laffan, Qatar. This plant, called Pearl GtL, produces up to 120,000 barrels per day [46]. Although CtL and GtL processes ensure less dependency on crude oil reserves, their potential to help mitigate climate change and global warming is less than limited. Secunda CtL, for instance, is reported to be the largest single site CO<sub>2</sub> emitter on the planet [93]. Therefore, using renewable resources, such as

biomass in BtL processes or renewable electricity and captured CO<sub>2</sub> in PtL processes as feedstock for syngas production, FT synthesis may produce more sustainable synthetic fuels. However, large-scale BtL plants have yet to be realized, and although a number of demonstration plants have been planned and funded in the EU many have been never finalized (e.g., Choren in Germany, Solena in UK, and Kaidi in Finland) [94]. Currently, TotalEnergies realizes a BtL pilot plant in Dunkirk, France, where lignocellulosic biomass is gasified to produce FT diesel and jet fuel. At the end of the project, the production is intended to be up scaled to industrial scale [95]. To the present day, PtL processes have also not progressed beyond demonstration scale. Since 2015 the German company sunfire produced about three tons of a synthetic oil called “Blue Crude” in a demonstration plant in Dresden using CO<sub>2</sub>, water, and renewable electricity. Together with Nordic Blue Crude, Climeworks, and others, sunfire is currently building a large-scale PtL plant in Herøya, Norway, with the goal to produce ten million liters of synthetic crude oil per year in the first stage. Within five years, the production capacity is planned to be up-scaled 20-fold to 200 million liters a year [96].

The FT process catalytically converts syngas with a typical molar H<sub>2</sub>/CO ratio of 2-2.2 to a variety of hydrocarbons, predominantly straight chain hydrocarbons such as olefins and alkanes. This hydrogenation of CO can be distinguished in high temperature Fischer-Tropsch (HTFT) applications using temperatures of 300-350 °C and low temperature Fischer-Tropsch (LTFT) applications using temperatures of 200-240 °C, both at operating pressures of usually 20-30 bar [45, 46]. The FT reactions are highly exothermic releasing abundant process. The product range synthesized by FT synthesis is remarkably diverse and the specific product distribution varies based on the actual reaction conditions, such as catalysts, temperature, pressure, gas velocity, and H<sub>2</sub>/CO ratio [97].

### Catalysts and Converters

The FT synthesis requires a catalyst to produce hydrocarbons from syngas. Iron (Fe) catalysts can be used in HTFT processes which produce shorter chain olefins as main product. Cobalt (Co) is not suited as catalyst for HTFT due to the excessive methane production at elevated temperatures. The HTFT route is often used to process syngas with low H<sub>2</sub> content from coal or biomass gasification, as Fe also catalyzes the WGS reaction which adjusts the H<sub>2</sub>/CO ratio to the correct range. Since Fe of course is also active for rWGS, it is also promising for PtL applications using CO<sub>2</sub> based feed gas from CC and water electrolysis [45]. LTFT processes are able to use either Fe or Co catalysts to yield high-molecular-mass paraffinic hydrocarbons called waxes as main product. Although Fe is less expensive, the higher activity and selectivity towards linear hydrocarbons in addition to their higher stability makes Co often the catalyst of choice in LTFT, especially for high H<sub>2</sub>/CO ratio syngas conversion or in PtL applications where syngas is produced by co-electrolysis of CO<sub>2</sub> and water [45, 46]. The rapid and sufficient removal of process heat is of vital importance in FT reactors to avoid catalyst overheating and deactivation. The two major classes of FT converters are the fixed-bed reactor and the fluidized bed reactor. The choice of reactor design depends first and foremost on the operating conditions and the target products [84]. In fixed-bed reactors the catalyst particles are packed into narrow tubes which are enclosed in an outer shell, and the tubes are immersed in water as heat transfer medium. This reactor type is used for LTFT processes such as the Pearl GTL plant in Qatar [46]. In circulating fluidized bed processes fine Fe catalyst particles are entrained by a high velocity stream of syngas. This type of reactor was used for the HTFT processes in SASOL II and SASOL III [92, 98].

Table 6-9: FT syncrude compositions on a mass basis [99].

Compound		FT syncrude composition [wt. %]		
		Fe-HTFT	Fe-LTFT	Co-LTFT
<b>Gaseous products (C1-C4)</b>	Methane	12.7	4.3	5.6
	Ethane	4.5	1.0	1.0
	Ethene	5.6	1.0	0.1
	Olefins	21.2	6.0	3.4
	Paraffins	3.0	1.8	1.8
<b>Naphtha (C5-C10)</b>	Olefins	25.8	7.7	7.8
	Paraffins	4.3	3.3	12.0
	Aromatics	1.7	0	0
	Oxygenates	1.6	1.3	0.2
<b>Distillate (C11-C22)</b>	Olefins	4.8	5.7	1.1
	Paraffins	0.9	13.5	20.8
	Aromatics	0.8	0	0
	Oxygenates	0.5	0.3	0
<b>Wax</b>	Olefins	1.6	0.7	0
	Paraffins	0.4	49.2	44.6
	Aromatics	0.7	0	0
	Oxygenates	0.2	0	0
<b>Aqueous product</b>	Alcohols	4.5	3.9	1.4
	Carbonyls	3.9	0	0
	Carboxylic Acids	1.3	0.3	0.2

The raw product of FT synthesis is often referred to as syncrude due to the fact that it is a complex mixture of a variety of hydrocarbon and oxygenate compounds, as is fossil crude oil. The primary compounds present in FT syncrude are paraffins and olefins, but also oxygenates such as alcohols and carbonyls are present [97]. Only a small portion of syncrude, called straight run syncrude, has the correct chain-length distribution for being directly applicable as transportation fuel [99]. The majority has to be converted via refinery processes to meet the desired product requirements.

### Syncrude Upgrading

Depending on the catalyst system and the exact operating conditions of the FT synthesis the product distribution greatly varies in terms of chain-length, the amount of saturated and unsaturated hydrocarbons, and the presence of oxygenated compounds (Figure 6-10). Hence, the refinery designs must be optimized to the respective FT synthesis. HTFT syncrude primarily consist of light, linear olefins and paraffins are only a minor component. Some aromatic compounds are present and oxygenates are present mainly in the aqueous product. Long-chain paraffins are the main compounds presents in LTFT syncrude with very small amounts of aromatic compounds in the products of both Fe-LTFT and Co-LTFT. The olefin content is low in Fe catalyzed syncrude, and even lower if Co-based catalysts are used. The small amount of oxygenates consist primarily of alcohol and carboxylic acids [99].

It has been reported that for FT gasoline production the best option is an iron catalyzed HTFT synthesis at temperatures of about 340 °C, as is produces close to 40 % straight run naphtha [98]. However, this straight run naphtha is not suitable for use in a gasoline engine as due to highly linear carbon chains the octane value is very low. Therefore, the naphtha fraction is converted into branched hydrocarbons by hydro-isomerization or aromatic compounds by catalytic reforming. The C<sub>2</sub>-C<sub>4</sub> gaseous fraction is highly olefinic and can be converted to gasoline by olefin oligomerization reactors with a solid phosphoric acid

catalyst. The kerosene fraction ( $C_{11}$ - $C_{14}$ ) and distillate fraction ( $C_{15}$ - $C_{22}$ ) can be either hydrogenated to be used as jet fuel or diesel, respectively, or hydrocracked into shorter chain-length to increase the gasoline yield. The FT gasoline produced by HTFT, and subsequent refining steps usually meets the specifications set in DIN EN228 for unleaded automotive petrol fuel. The research octane number and the motor octane number are in the range of 97-98 and 89-90, respectively. The density is the range of  $740 \text{ kg}\cdot\text{m}^{-3}$  [100]. The undesired properties of FT products for gasoline production, namely the high linearity of hydrocarbon chains together with the very low aromatics content prove to be very advantageous for FT diesel production. The recommended process is a LTFT synthesis using a cobalt based catalyst, since it produces about 20 % of straight run diesel which is free from aromatic compounds and sulfur, as well as a highly paraffinic wax fraction [98]. This wax fraction which makes up for usually 45-50 % of the LTFT syncrude is generally converted into diesel by mild hydrocracking using platinum, palladium, or bimetallic compounds as catalysts at 250-300 °C in hydrogen rich atmosphere of 30-50 bar [46]. The final FT diesel has a cetane number of about 70, which is well above the minimum specification of 51 set in DIN EN590 [101].

### 6.3.5.3.2 Methanol Pathways

Methanol is one of the most produced chemicals in the world with a worldwide production capacity just shy of 160 million tons per year in 2020. The global production is forecast to grow to over 300 million tons in 2030 [102, 103]. It is used as a platform chemical in the chemical industry to produce substances such as formaldehyde, acetic acid, and methyl tertiary-butyl ether, which is mainly used as an antiknock agent additive in gasoline [104]. Methanol can also be used as a fuel, either through blending with conventional gasoline or alone in modified combustion engines [88]. It can be also further processed to dimethyl ethers, polyoxymethylene ethers, or hydrocarbons via the MtG route [45, 89].

Methanol is currently produced at industrial scale almost exclusively from syngas derived from fossil fuels such as natural gas and coal [67]. Of course, syngas derived from renewable resources can also be used in this synthesis making methanol a fuel candidate for decarbonized transport sector [105]. The direct hydrogenation of  $\text{CO}_2$  using hydrogen from renewable resources can be a utilization of captured  $\text{CO}_2$  from either air or point sources [45].

#### Methanol Production from Syngas

The synthesis of methanol is an industrial process since 1923, when BASF started operating its first plant [45] (TRL = 9). The BASF process was operated at high pressures of 250-300 bar and high temperatures above 300 °C using a  $\text{ZnO}/\text{Cr}_2\text{O}_3$  catalyst. The economically demanding high pressure conditions necessitated by the relatively low catalyst activity led to the development of new Cu-ZnO catalysts that were able to catalyze the methanol synthesis from syngas at lower pressures of 50-100 bar. The temperatures applied in the low-pressure process are above 200 °C for optimal activity of the Cu catalyst but are limited by its thermal stability to under 300 °C [88]. Today, the low-pressure process is exclusively used to produce methanol using a  $\text{Cu-ZnO}/\text{Al}_2\text{O}_3$  catalyst [106]. This catalyst shows a selectivity of over 99 % for methanol synthesis and so the content of impurities, except for water, is generally very low in raw methanol [45].

The gas feed for methanol synthesis is syngas with a  $\text{H}_2/\text{CO}$  ratio of 2. However, small amounts of  $\text{CO}_2$ , usually around 3-10 vol% are added to the syngas stream since the reaction is significantly accelerated in the presence of  $\text{CO}_2$  [83]. Methanol is produced by the direct hydrogenation of  $\text{CO}_2$  producing water as by product [45]. The water produced in this reaction facilitates the formation of  $\text{CO}_2$  from CO via the WGS that in turn is hydrogenated to methanol [55].



## Methanol from Direct Hydrogenation of CO<sub>2</sub>

As mentioned above, methanol synthesis on industrial scale uses syngas, predominantly from fossil sources. However, since the 1990s, processes for the direct hydrogenation of CO<sub>2</sub> with H<sub>2</sub> to methanol without using syngas are heavily investigated. Demonstration scale plants have proven the technical feasibility of this methanol production route [102] (TRL = 7-8). For example, CRI together with eight partners realized a CO<sub>2</sub> to methanol plant in Niederaussem, Germany in 2019 within a technology development project called MefCO<sub>2</sub> under the EU Horizon 2020 Framework Program. MefCO<sub>2</sub> captures CO<sub>2</sub> from a thermal power plant and converts it to methanol with hydrogen derived from water electrolysis using surplus electricity from renewable resources. The production capacity is one ton per day [107].

The direct hydrogenation of CO<sub>2</sub> is less exothermic than the hydrogenation of CO, thus less cooling of the reactor vessel is required. Also, avoiding an additional unit for syngas production via rWGS has great economic value for PtL processes using captured CO<sub>2</sub> and hydrogen from water electrolysis powered by renewable energy. It has been reported that the ideal H<sub>2</sub>/CO<sub>2</sub> ratio for direct CO<sub>2</sub> conversion to methanol is in the range of 3-5 [55]. However, the water formed during this reaction is not removed via the rWGS in the absence of CO and deactivates active sites on the Cu-ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst used in the syngas process. Water is also a strong oxidant for metals at elevated temperatures, leading to metal oxide formation and therefore further loss of active sites on the catalyst surface. A third of the hydrogen in the feed gas is not converted to methanol but is bound in the water molecules in the product mixture [88].

To overcome the limitations of the catalyst system experienced by the direct CO<sub>2</sub> hydrogenation, the key approach is the modification of the catalyst to enhance the surface area and the active sites as well as the robustness against water deactivation, since for the removal of water during the course of the reaction, no significant solution has been presented yet [88].

## Reactor Designs

The conversion of CO and CO<sub>2</sub> to methanol are both exothermic reactions and lead to a decrease in volume on the product side. Therefore, methanol production is favored by high pressure and low temperature. The need for efficient temperature control as well as manufacturing constraints of the pressure vessel are the major challenges in the reactor designs for this synthesis. The industrial scale methanol reactor development for syngas to methanol conversion follows the trend of increasing production capacities to decrease the specific cost of methanol production. Current converters are predominantly fixed bed reactors [45]. While for methanol synthesis processes from syngas the effort to increase the product capacity of the converter is economically beneficial, the direct hydrogenation of CO<sub>2</sub> pursues a different goal. Here, small-scale plants are of interest to produce methanol from CO<sub>2</sub> streams captured from point sources or directly from the air. Those plants should be ideally in close proximity to renewable energy sources needed for sustainable hydrogen production through water electrolysis. Therefore, efforts are necessary to adopt above large-scale converter technologies to the needs of small-scale applications [45].

## Methanol Upgrading

When comparing the composition of raw methanol produced from CO<sub>2</sub> with that of methanol produced from a syngas feed the significantly higher water content of the CO<sub>2</sub> based mixture becomes apparent (Table 6-10). The formation of impurities as higher alcohols or other oxygenates are, however, lower than in the syngas derived mixture, representing an even higher selectivity for methanol.

Table 6-10: Raw methanol compositions of methanol syntheses using CO-based syngas and CO<sub>2</sub>-based feed gas at 250 °C [45].

Components	CO-based syngas	CO <sub>2</sub> -based feed gas
Methanol [wt%]	84.5	63.7
Water [wt%]	15.4	36.2
n-Paraffins [ppm]	78	0
Higher alcohols [ppm]	626	89
Esters [ppm]	582	145
Ketones [ppm]	24	0
Dimethyl ether [ppm]	61	14
Methanol selectivity [%]	99.84	99.96

For fuel grade methanol with purities > 99 % the raw methanol is upgraded by using a single distillation column to remove water. Other impurities as higher alcohols or other oxygenates do not pose a problem and are considered beneficial due to the higher energy content. To produce methanol with a purity > 99.85 % (Grade A) for synthesis purposes a series of distillation columns is required [55].

### 6.3.5.3.3 DME Synthesis

Dimethyl ether (DME), or methoxy methane is the simplest ether and a colorless, non-toxic, non-carcinogenic, and non-mutagenic gas at standard conditions. It can easily be liquified at pressures of 5 bar and is therefore often handled and stored as a liquid. Since DME carries an oxygen atom in the molecule and possesses no direct C-C bonds, but only C-H and C-O bonds, its combustion produces lower emissions of CO and unburned hydrocarbon than compared to conventional diesel fuel [108]. That, and its high cetane number of in the range of 55-60 makes it a promising candidate for a renewable diesel substitute if it is produced from renewable resources [109]. Various routs depending on the feedstock for the synthesis of DME are available and they are generally classified as indirect processes using methanol as feedstock and direct processes producing DME directly from syngas (Figure 6-17).

#### DME Synthesis from Methanol

The synthesis of DME through the dehydration of methanol is currently the only large-scale production of DME (TRL = 9). This exothermic reaction is used in production sites generally in the vicinity of methanol plants. The reaction is usually catalyzed by solid acid catalysts such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or ZSM-5 zeolite in fixed bed reactors that are operated at temperatures in the range of 250-400 °C and pressures of 5-20 bar [45, 110]. The feed stream is usually vaporized fuel grade methanol that is partly converted to DME, water, but also gaseous impurities like CH<sub>4</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>. The conversion rate per pass is around 70-80 % and unreacted methanol is separated by distillation and recycled back to the feed stream. The purification of DME is carried out by a two-step distillation, where in the first column DME and other gases are separated from the water and residual methanol phase, and the gases are removed in the second flash separation step. Capacities of commercial reactors for the DME synthesis from methanol are in the range of several 100,000 tons of DME per year [45].

#### DME Synthesis from Syngas

Recently, a process has been developed for the production of DME directly from syngas where all the single reaction steps for methanol synthesis, rWGSR, and methanol dehydration occur in a system of bifunctional catalysts in a single reactor vessel at the same time. This has a tremendous effect on the syngas conversion rate compared to the DME synthesis from methanol route. First, the methanol being the product of the syngas conversion is consumed by the dehydration reaction to DME, and thus shifts



the equilibrium of the methanol synthesis to the product side. Also, the water formed in the dehydration reaction is removed by the rWGSR which protects the active sites on the catalyst surface from degradation. The reactor design often follows the fixed bed concept where the syngas fed to the converter at operating conditions of usually 200-300 °C and 30-70 bar has a H<sub>2</sub>/CO ratio of 1-2 [45]. The product upgrade is far more complex for this DME pathway since the product mixture consists of DME, methanol, CO<sub>2</sub>, H<sub>2</sub>O, and unreacted syngas. Of all these compounds, the removal of CO<sub>2</sub> from DME has proven extremely difficult and it requires great efforts to achieve high purities. First, unreacted syngas is separated at temperatures of about – 40 °C from the liquid products in a cryogenic liquid-gas separator and cycled back to the DME synthesis reactor. The CO<sub>2</sub> is mostly dissolved in DME and scrubbed in a CO<sub>2</sub> separator. DME is obtained by a distillation step where it is separated from methanol and water. The methanol is recovered and led back to the DME synthesis reactor by a second distillation step. Hence, the benefit of having the simplicity of just one reactor vessel in the synthesis process is traded for a rather complex product upgrade [110].

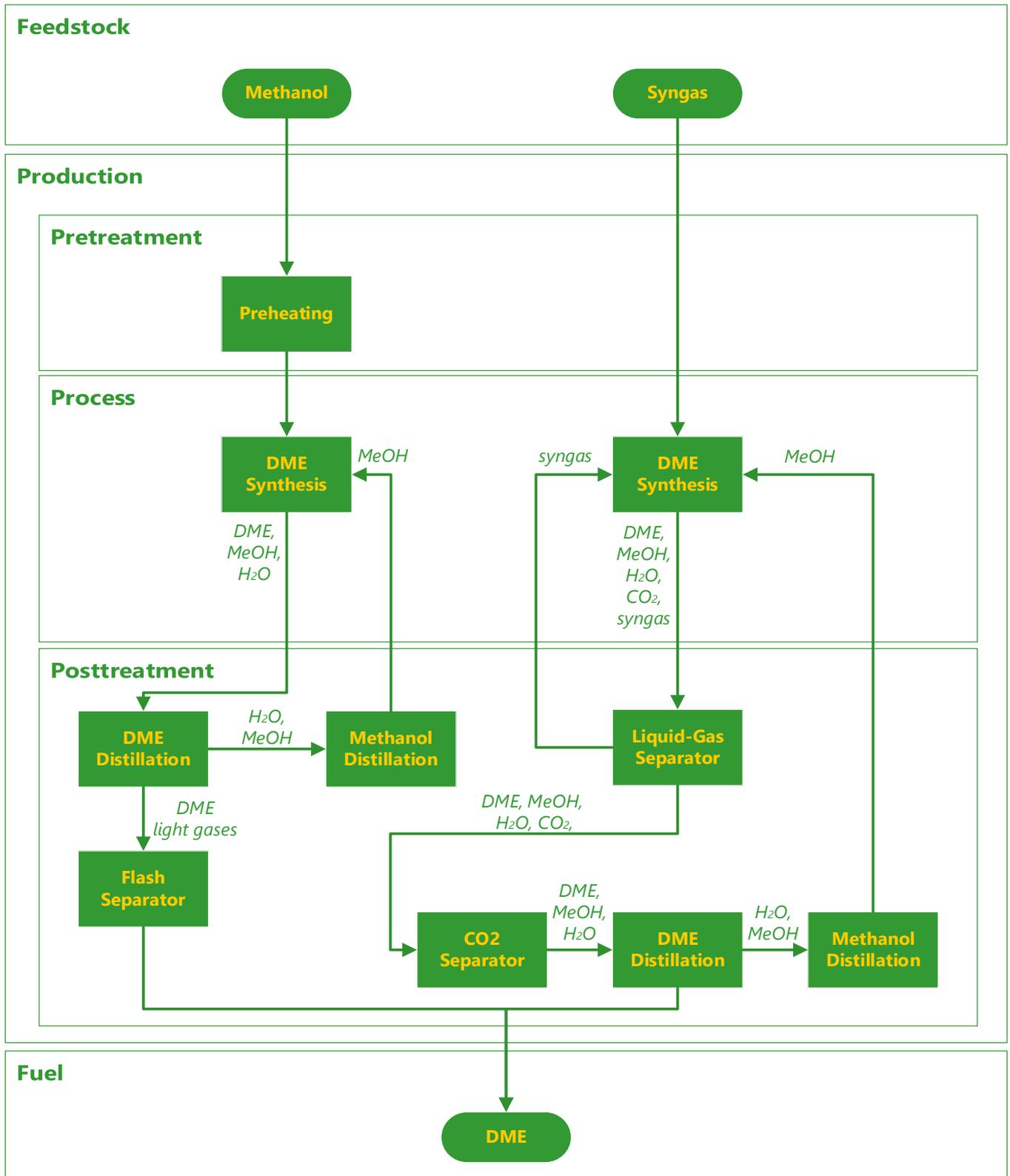


Figure 6-17: General scheme of the indirect DME production pathway from methanol and the direct DME production pathway from syngas.

### 6.3.5.3.4 OME Synthesis

As a drop-in fuel for diesel engines or as an additive for conventional diesel OME<sub>3-5</sub> has received considerable attention in the past years. Methanol can be regarded as the starting material for the production of this polyoxymethylene dimethyl ether [111]. It is usually used as a mixture of varying chain-

length, typically with three to five repeating units called OME<sub>3-5</sub>. This chain-length yields properties very similar to conventional diesel in terms of boiling range, viscosity, and cetane number [112]. The high inherent oxygen content of polyoxymethylene dimethyl ethers lead to advantageous combustion properties in diesel engines [113]. Same as DME, OMEs have no direct C-C bond and burn almost soot free [86].

The production of renewable OME<sub>3-5</sub> is still a subject of research and no commercial plant has been realized yet (TRL = 4 [114]). However, demonstration plants such as the one operated by TUM at Straubing, Germany prove the technical feasibility of the production process. This demonstrator was funded by the German Bundesministerium für Bildung und Forschung within the NAMOSYN (Nachhaltige Mobilität durch synthetische Kraftstoffe) project and started operation in 2021. It is the first production facility in Europe that can continuously produce OME<sub>3-5</sub> from renewable resources [115].

Various pathways for OME<sub>3-5</sub> synthesis are available that can be distinguished in anhydrous and aqueous pathways (Figure 6-18). Both pathways require a methyl-capping source and a monomer source for oxymethylene groups. The capping sources for the methyl end group described in literature are methanol, DME, and dimethoxymethane (DMM). Monomer sources are usually formaldehyde or trioxane [112]. All of those compounds can be produced from methanol [111].

Formaldehyde can be produced from methanol by a partial oxidation with air, either using a silver catalyst or a molybdenum-iron catalyst. The silver-catalyzed process is more energy demanding, due to the high process temperatures in the range of 600-700 °C, compared to the required 300-400 °C of the molybdenum-iron route [116].

DMM, or methylal, is the simplest polyoxymethylene dimethyl ether (OME<sub>1</sub>) and can be synthesized from a solution of methanol and formaldehyde with the help of ZnCl<sub>2</sub> or FeCl<sub>3</sub> catalysts. This reaction can be realized in a reactive distillation column with three to five reactor units. However, DMM purities of only 98 % can be reached using this process. High purity DMM of 99.5 % can be obtained by a different process using a tubular fixed bed reactor and a subsequent purification of DMM by two distillation columns operating at different pressures [116].

Trioxane is a cyclic compound that is conventionally synthesized from an aqueous formaldehyde solution via a sulfuric acid catalyzed reaction below 100 °C. The trioxane is then extracted from the product stream using halogenated solvents which are then removed by a distillation step. To avoid the employment of halogenated solvents, a series of three distillation columns can be used for purification [116].

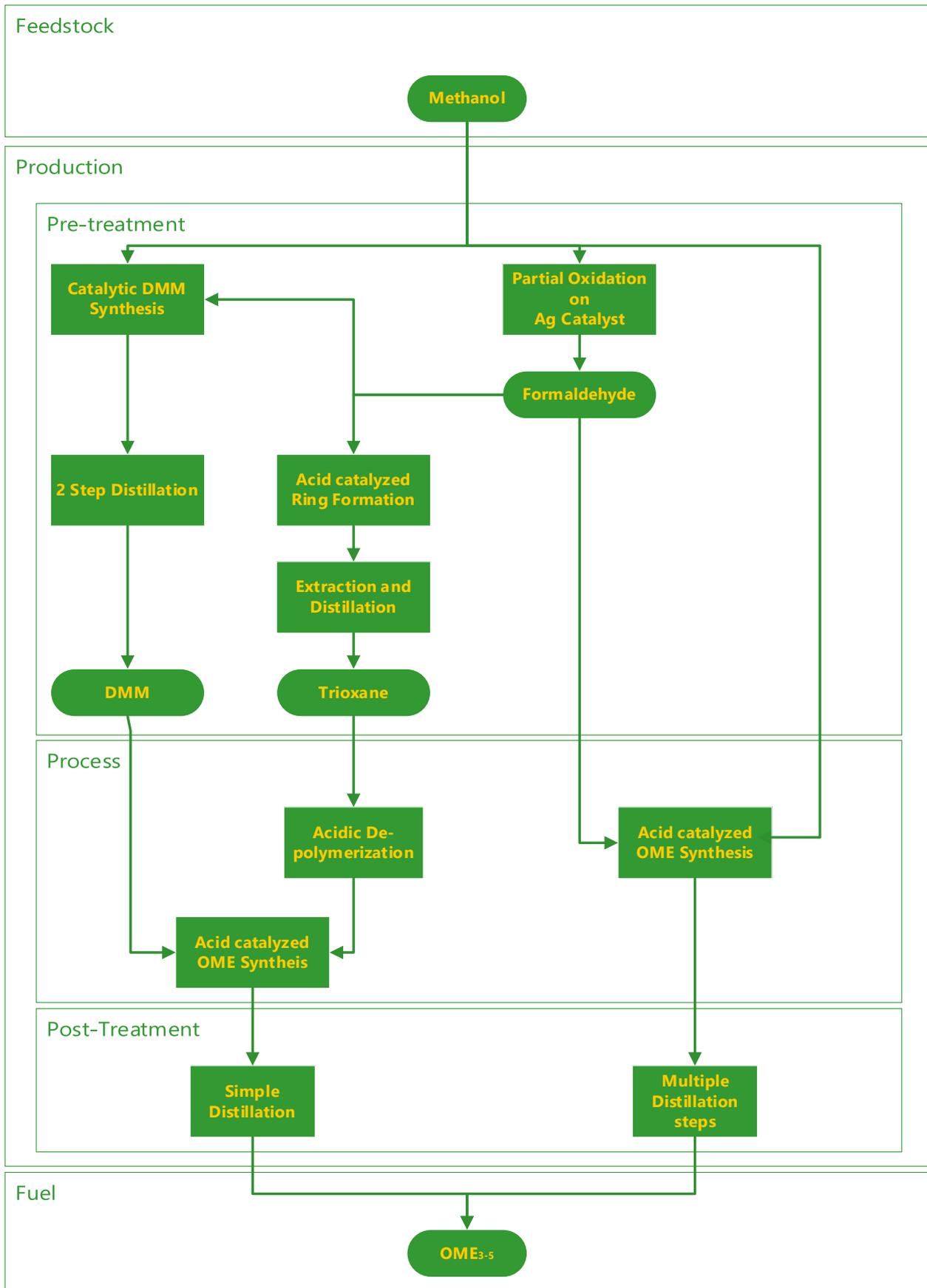


Figure 6-18: General Scheme of anhydrous and aqueous pathways for the synthesis of OMEs.

### Non-aqueous OME Synthesis

In the anhydrous pathway for OME production, trioxane is usually employed as a monomer source. In an acidic depolymerization reaction the trioxane molecule is broken down to 3 formaldehyde molecules, which in turn react with DMM to yield OME<sub>2</sub>. The reaction is carried out slightly elevated temperatures of 50-100 °C, usually in fixed bed reactors. The yield of OME<sub>1-5</sub> is typically around 70 % using the non-aqueous pathway. The advantages of this strategy are a high OME selectivity and low content of by-products in the product mixture. This mixture is usually purified by simple distillation measures. However, the preparation of trioxane and DMM require multiple synthesis steps from methanol as platform chemical and so a less complicated route including less steps would seem desirable [117].

### Aqueous OME Synthesis

The direct synthesis of OMEs from methanol and formaldehyde enables the production of OME from simple starting materials. This reaction is usually carried out in batch reactors using acidic catalysts [113]. In a reaction cascade methanol reacts with formaldehyde to OME, forming water as by-product. Although the utilization of simple starting materials seems favorable, this pathway only yields product mixtures with an OME<sub>1-5</sub> content around 35 %, and the water as well as other by-products formed in the reaction cascade necessitate rather elaborate purification steps [117].

Although CtL and GtL processes ensure less dependency on crude oil reserves, their potential to help mitigate climate change and global warming is less than limited. Secunda CtL, for instance, is reported to be the largest single site CO<sub>2</sub> emitter on the planet [93]. Therefore, using renewable resources, such as biomass in BtL processes or renewable electricity and captured CO<sub>2</sub> in PtL processes as feedstock for syngas production, FT synthesis may produce more sustainable synthetic fuels. However, large-scale BtL plants have yet to be realized, and although a number of demonstration plants have been planned and funded in the EU many have been never finalized (e.g., Choren in Germany, Solena in UK, and Kaidi in Finland) [94]. Currently, TotalEnergies realizes a BtL pilot plant in Dunkirk, France, where lignocellulosic biomass is gasified to produce FT diesel and jet fuel. At the end of the project, the production is intended to be up scaled to industrial scale [95]. To the present day, PtL processes have also not progressed beyond demonstration scale. Since 2015 the German company sunfire produced about three tons of a synthetic oil called "Blue Crude" in a demonstration plant in Dresden using CO<sub>2</sub>, water, and renewable electricity. Together with Nordic Blue Crude, Climeworks, and others, sunfire is currently building a large-scale PtL plant in Herøya, Norway, with the goal to produce ten million liters of synthetic crude oil per year in the first stage. Within five years, the production capacity is planned to be up-scaled 20-fold to 200 million liters a year [96].

## 7 RESULTS AND DISCUSSION

This section presents the results of the literature screening. The main focus of this chapter is the GWP of the previously established fuel classifications. Synthetic fuel production process steps are discussed in more detail. Projections are presented separately. The results for midpoint indicators other than GWP are based on a smaller available data sample and are therefore presented in a more qualitative manner. Finally, the most impactful systematic choices concerning GWP are examined.

Results are presented in boxplots, in which locality, dispersion and shape measurements are displayed. A brief explanation these plots is given here.

- **Locality Measures:** Mean value ( $x$ ), median (horizontal line)  
These parameters provide information about a central tendency of the dataset. The mean value is heavily influenced by outliers, therefore a parameter with a high robustness against outliers, the median, will be a better representation of a typical value. The median divides the dataset in its lower and higher half.
- **Dispersion Measures:** Interquartile range (IQR), total range  
The total range is defined by the minimum and maximum values of a dataset. The IQR is the difference between the 75<sup>th</sup> (Q3) and 25<sup>th</sup> (Q1) percentiles of the dataset. As it contains 25 % of the data points above and below the median, it provides information on the range in which a typical value can be expected. Furthermore, the IQR allows to identify outliers, which are above the threshold of  $Q3+1,5*IQR$  or below  $Q1-1.5*IQR$ .
- **Shape Measurements:** Empiric skewness  
The skewness is visualized in the plot and can be estimated by the position of the median in the IQR. The skewedness gives information about tendencies towards higher (negative/left skewness) or lower (positive/right skewness) values within the dataset.

This method is chosen to emphasize that the results of this study are not single values that are fit to serve as a baseline for EcoFuel. It rather shows a range of typical GWP values for different fuels. The aggregation to average values or the presentation of single studies results is avoided due to the high methodological uncertainties related to the analyzed LCA studies analyzed. The presented ranges for carbon footprints do not only originate from methodological differences in studies but they also contain a variety of different production scenarios. In addition, none of the analyzed studies are based exclusively on primary data.

In total 258 GWP values have been extracted from the found literature. Figure 7-1 shows the distribution of the GWP data by fuel classes. The exact composition of the data points is presented in Table 7-1. The outliers from Figure 7-1 do not only originate from the aggregation of different fuel pathways into fuel classes, but also from systematic and methodological differences between studies. The outliers are analyzed in detail in the following chapters.

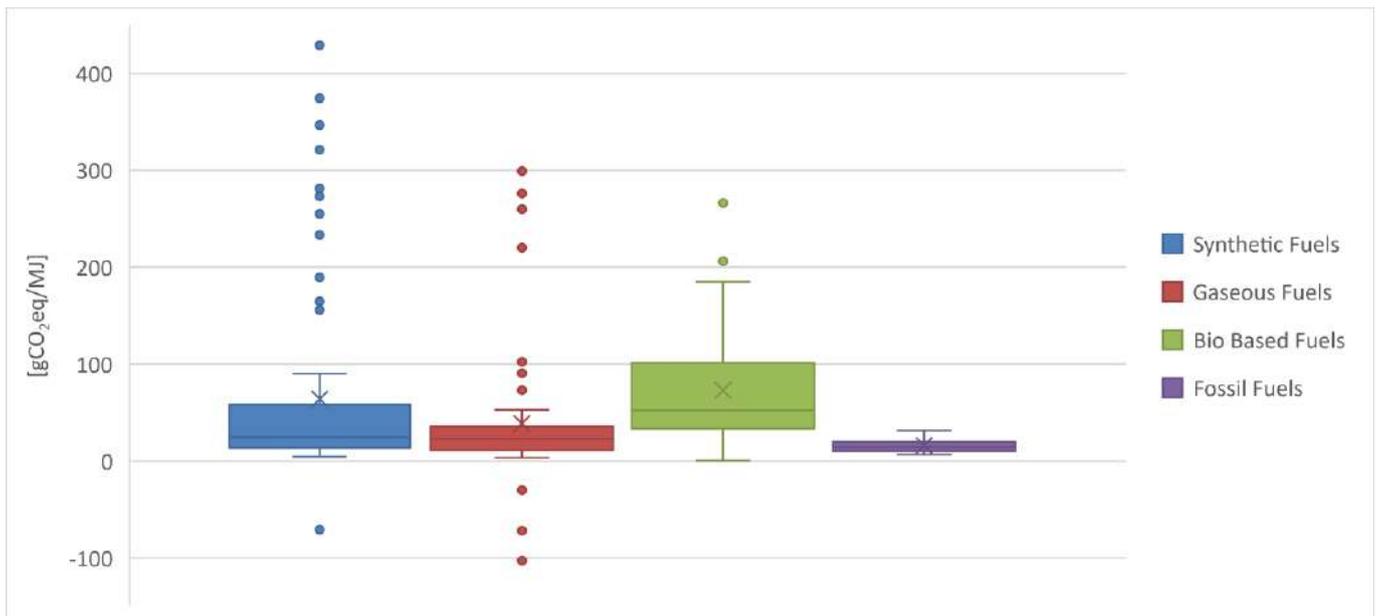


Figure 7-1: Boxplots of the GWP for the fuel classifications, number of data points N=258, without data point projections.

Table 7-1: Selection of statistical parameters of the fuel Classifications, without projected data points.

Fuel Classification	Data Points N [#]	Share [%]
Synthetic Fuels	79	30.62
Bio-based Fuels	88	34.10
Gaseous Fuels	68	26.35
Fossil Fuels	23	8.93
Sum	258	100

Table 7-2: Selection of statistical parameters of the fuel Classifications, without projected data points.

Fuel Classification	Min Value [gCO <sub>2</sub> eq/MJ]	Max Value [gCO <sub>2</sub> eq/MJ]	Median [gCO <sub>2</sub> eq/MJ]	Mean Value [gCO <sub>2</sub> eq/MJ]	Q1 [gCO <sub>2</sub> eq/MJ]	Q3 [gCO <sub>2</sub> eq/MJ]
Synthetic Fuels	-70.82	429.00	24.73	64.21	13.55	58.70
Bio-based Fuels	0.40	267.00	56.00	75.23	34.70	103.00
Gaseous Fuels	-103.00	301.97	22.80	38.86	11.17	35.93
Fossil Fuels	6.70	31.50	14.20	15.86	10.50	20.00

Fossil FPPWs have the smallest IQR of all fuel classifications. The dataset is moderately positively skewed. The representation of the fossil fuel data group is roughly 8.8 %.

bio-based fuels have the largest IQR with only a few outliers are included in the dataset. The data points have a tendency towards the Q1 and are highly skewed. The mean value is greatly influenced by the top end of the distribution. The share of the group is 35.5 % which is the largest throughout all the classes.

Gaseous fuels are represented by 25.95 % of the data points in the whole dataset and show a narrow IQR. The dataset of gaseous fuels has a positive skewness.

synthetic fuels are represented by the second highest share of the dataset with 29.77 %. This dataset has the highest total range and is highly positively skewed.

The assumption can be made that facility related environmental impacts are declining with economies of scale and higher process efficiencies. However, data on TRL levels and process efficiencies is scarce. The most popular alternative FPPWs are used on industrial scales and have TRLs of 8-9. Less mature technologies such as pyrolysis or rWGS are still in development and their TRLs don't go beyond 6. The

correlation of TRL levels and GWP results is infeasible because the effects of other influencing factors (i.e.: system boundaries, crediting, LUC...) could not be clearly separated from TRL values.

## 7.1 Fossil Fuels

Due to their high technological maturity and low energy demand in production, traditional fossil fuels have a comparatively low carbon footprint in production. On average diesel performs about the same as gasoline from a WTT viewpoint. The production routes for diesel and gasoline are very similar in terms of extraction and distillation. They differ only in the aftertreatment processes, which have low impact on the GWP result. An overview of the WTT GWP results for fossil fuels is shown in Figure 7-2 and Table 7-3.

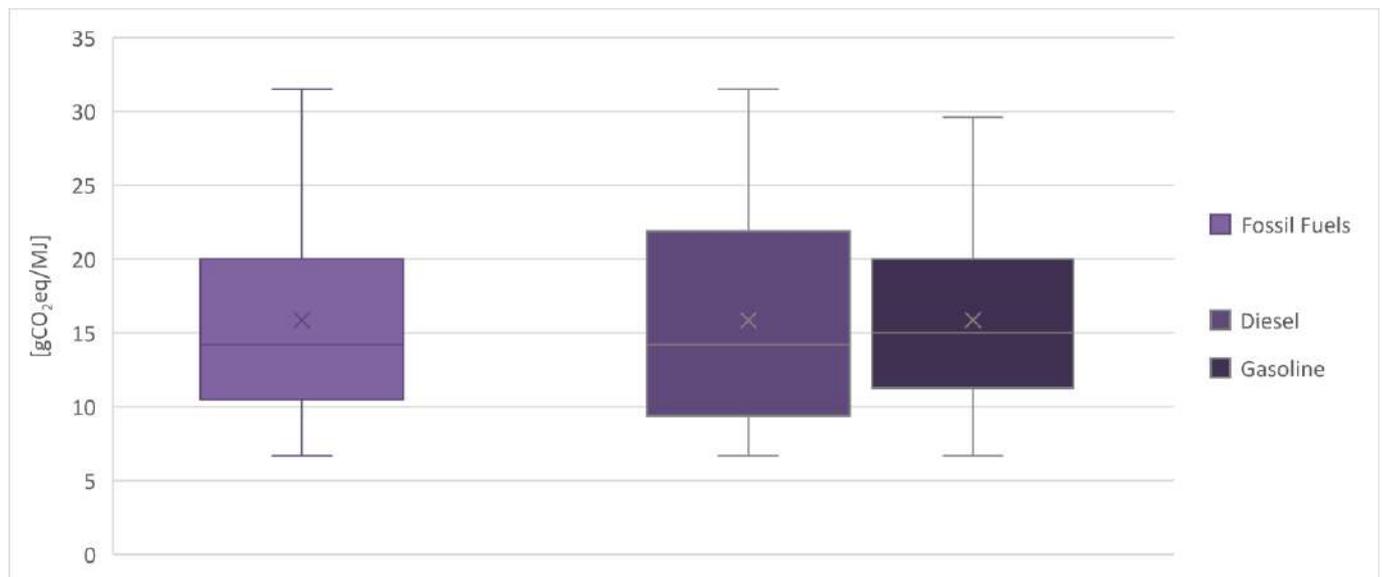


Figure 7-2: WTT GWP results for fossil fuels. Number of data points N=23.

Table 7-3: Overview of WTT GWP results for fossil fuels.

Fuel Type	Min Value [gCO <sub>2</sub> eq/MJ]	Max Value [gCO <sub>2</sub> eq/MJ]	Median [gCO <sub>2</sub> eq/MJ]	Mean Value [gCO <sub>2</sub> eq/MJ]	Q1 [gCO <sub>2</sub> eq/MJ]	Q3 [gCO <sub>2</sub> eq/MJ]
<b>Fossil Fuels</b>	6.70	31.50	14.20	15.86	10.50	20.00
<b>Diesel</b>	6.70	31.50	14.20	15.84	9.89	21.90
<b>Gasoline</b>	6.70	29.60	15.00	15.88	11.25	20.00

The difference in carbon footprints seems to be marginal across most studies. [118] conducted a detailed analysis on Swiss fuel supply, identifying crude oil production and refinery operation to be the main carbon footprint drivers, accounting for 79.5 % of the WTT footprint for gasoline and 87.5 % for diesel respectively. Transport and distribution make up the rest.

The ranges for fossil fuels serve as a baseline for comparison with alternative fuels. Most data points were extracted from LCA studies which used them as reference values. Those pathways are often less detailed and fewer in number. Therefore, it is plausible that these values are underestimating GWPs. The prospection of new oil reserves as well as flaring at drill sites is often disregarded in LCAs. As sweet oil reserves decline and production tends to become more reliant on heavy crude oil, WTT carbon footprints for fossil fuels may rise due to higher efforts for sulfur removal. Blends tend to have a higher carbon footprint, the higher the share of bio-based fuel as shown in [119]. This is due to the lower WTT carbon footprint of CFFs. Based on the results of this study, this holds for synthetic fuels as well. If crediting is considered this might change since bio-based fuels and most synthetic fuels emit previously bound carbon

when combusted. The carbon footprint of blends, as well as the impact of blending itself may pose on fuel pathways, will not be evaluated further in this study.

## 7.2 Bio-based Fuels

The data for bio-based fuels WTT GWPs is summarized in Figure 7-3.

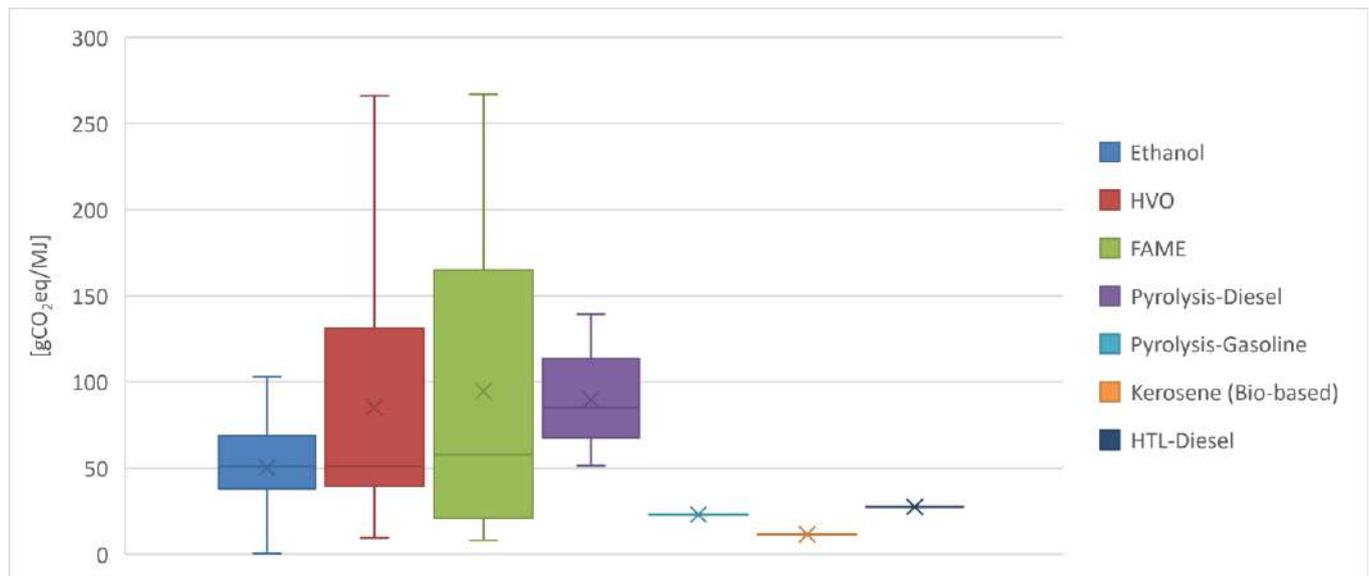


Figure 7-3: Boxplots of the different fuel types of bio-based fuels, number of data points N=88 (Ethanol N=32; HVO N=24; FAME N=23; Pyrolysis-Diesel N=6; Pyrolysis-Gasoline N=1; Kerosene N=1; HTL-Diesel N=1).

Table 7-4 Overview of WTT GWP results for bio-based fuels.

Fuel Type	Min Value [gCO <sub>2</sub> eq/MJ]	Max Value [gCO <sub>2</sub> eq/MJ]	Median [gCO <sub>2</sub> eq/MJ]	Mean Value [gCO <sub>2</sub> eq/MJ]	Q1 [gCO <sub>2</sub> eq/MJ]	Q3 [gCO <sub>2</sub> eq/MJ]
Ethanol	0.40	103.00	51.00	50.39	38.12	68.87
HVO	9.51	266.00	51.05	85.13	39.50	131.18
FAME	8.00	267.00	58.00	94.70	21.00	165.00
Pyrolysis-Diesel	51.50	139.25	85.13	89.86	67.66	113.63
Pyrolysis-Gasoline	23.10	-	-	-	-	-
Kerosene	11.50	-	-	-	-	-
HTL-Diesel	27.50	-	-	-	-	-

Table 7-5 shows the top end of the distribution for FAME and HVO, as they show the highest GWP in this class. LUC is identified to be the main influencing factor for oil-based bio-based fuels carbon footprints. This is due to the high LUC connected to oil crop production, which is shown in the according section.

Table 7-5: The influence of LUC on bio-based fuel carbon footprints.

Fuel Name	WTT [gCO <sub>2</sub> /MJ]	GWP	Feedstock	GWP from LUC [gCO <sub>2</sub> /MJ](WTT%)	Source
FAME	267		Palm Oil	231 (86.5 %)	[119]
HVO	266		Palm Oil	231 (86.8 %)	[119]
FAME	214		Palm Oil	~148 (69.2 %)	[2]
FAME	212		Soybean Oil	~153 (72.1 %)	[2]
HVO	210		Soybean Oil	150 (71.4 %)	[119]
FAME	208		Soybean Oil	150 (72.1 %)	[119]
HVO	206		Palm Oil	~146.5 (71.2 %)	[2]
FAME (w. CH <sub>4</sub> capture)	185		Palm Oil	~148 (80 %)	[2]
HVO (w. CH <sub>4</sub> capture)	176		Palm Oil	~146.5 (83.2 %)	[2]

In the case of the highest extracted values, a FAME (267 gCO<sub>2</sub>eq/MJ) and a HVO (266 gCO<sub>2</sub>eq/MJ) produced from palmoil, ILUC makes up 86.5 % and 86.8 % of the WTT carbon footprint [119]. It should be noted that [119] evaluates ILUC while [2] evaluates both DLUC and ILUC. In the latter publication, DLUC makes up the great majority of the GWP emerging from LUC. The lowest observed values also originate from [119] being ethanol from residues with 0.4 gCO<sub>2</sub>/MJ and energy crop with 3.6 gCO<sub>2</sub>/MJ. Most of the lowest GWP bio-based fuel pathways are FAMEs and HVOs. Those FPPWs utilize waste oils for production which are considered LUC free. Advanced bio-based fuels perform noticeably better in this context since their feedstocks are considered waste in the first place, therefore not leading to LUC emissions (or any other cultivation related emissions) but still binding carbon from the atmosphere. This is reflected in the data points on bio-based fuels, since most FPPWs on the low end of GWP utilize waste feedstocks. If those feedstocks get more popular in the future, this impact assessment might change as wastes from biomass production could then be categorized as byproducts instead of waste. This would lead to them being assigned the corresponding burden from plant cultivation [62].

The difference in the range of distributions between ethanol, HVO and FAME could very well be attributable to the much lower LUC burdens connected to sugar and starch rich plant cultivation, compared to oil crop cultivation. Although the average impact of LUC on them is lower, fermentation based FPPWs produce CO<sub>2</sub> as a byproduct. This is not necessarily a drawback, since ethanol fermentation plants emit nearly pure CO<sub>2</sub> which makes them a very attractive option for PSC. The impact of LUC on pyrolysis fuels GWPs is much lower as well, since they are produced from lignocellulosic biomass, which is in most cases considered a feedstock for advanced bio-based fuels. The GWP range for pyrolysis fuels is still higher than for ethanol since pyrolysis tends to be more energy intensive than fermentation.

Even though the main driver for WTT carbon footprints of bio-based fuels is the feedstock provision, process specific hotspots matter as well. HVO production utilizes hydrogen for hydrocracking. Carbon footprints of hydrogen production vary widely depending on energy source and feedstock type. FAME production on the other hand uses catalyst leach for transesterification. The impacts of process specific differences in FPPWs are depicted in much less detail than feedstock specific differences in the analyzed LCAs. Crediting can in some cases change results drastically as well, and there seems to be no consensus in literature on how to exactly approach it. The extent to which crediting can impact LCA results will be discussed in detail in the corresponding chapter. Another important aspect of biogenic feedstock production, which will not be discussed in detail, is water usage. Although water consumption of bio-based fuel production is most likely the highest, synthetic fuel production, especially hydrogen production, can pose a significant burden on fresh water consumption as well.

The approach to waste management can lead to additional emissions, since composting of biomass residues again leads to the emission of CH<sub>4</sub> and CO<sub>2</sub>. In the case of palmoil based bio-based fuel production

[120] found that the usual practice of dumping the empty fruit bunches back on the field leads to noticeably higher emissions than composting. In addition, it is stated that wastewater treatment is important as well. Oil mill effluent storage leads to emissions, which can be captured and reused.

### 7.3 Synthetic Fuels

Synthetic fuels divided into their formerly established subcategories of SynBio, SynNoBio and SynFoFuels. An overview of the WTT GWP results for those fuel classes is shown in Table 7-6.

Table 7-6: Overview of WTT GWP results for the subcategories of synthetic fuels.

Fuel Type	n [#]	Share [%]	Min Value	Max Value	Median
SynBio Fuel	22	27.85	4.43	43.47	13.17
SynFo Fuel	7	8.86	22.11	281.39	155.65
SynNoBio Fuel	50	63.29	-70.82	429	29.42

Since data on SynFo fuels is scarce, they will be evaluated in less detail. Synthetic fuels relying at least partially on fossil-derived feedstocks are not uncommon, since steam methane reforming is still by far the most popular way of producing hydrogen. Still, most evaluated LCA studies assess FPPWs using hydrogen from water electrolysis or biogas reforming. Due to the lack of data, WTT GWP results for SynFo fuel are only presented in the above-mentioned table.

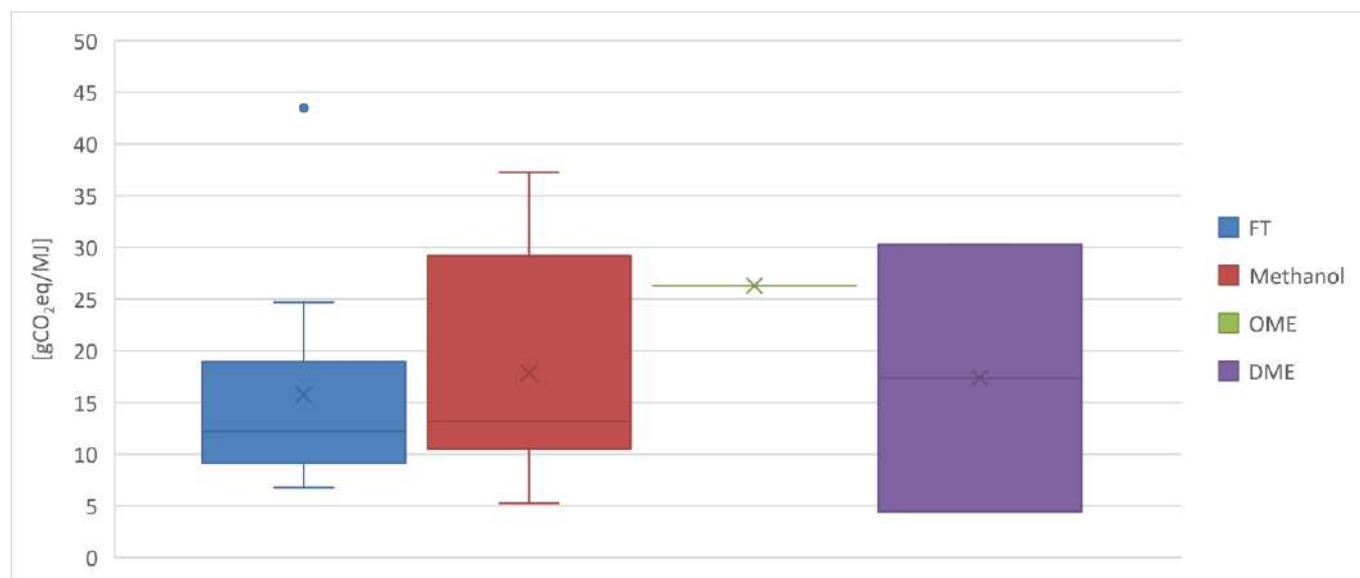


Figure 7-4: WTT GWP results for SynBio fuels. Number of data points N=22 (FT N=10; Methanol N=9; OME N=1; DME N=2).

Table 7-7: Overview of WTT GWP results for SynBio fuels.

Synthesis process	Min Value [gCO <sub>2</sub> eq/MJ]	Max Value [gCO <sub>2</sub> eq/MJ]	Median [gCO <sub>2</sub> eq/MJ]	Mean Value [gCO <sub>2</sub> eq/MJ]	Q1 [gCO <sub>2</sub> eq/MJ]	Q3 [gCO <sub>2</sub> eq/MJ]
FT	6.79	43.47	12.23	15.71	9.13	18.93
Methanol	5.25	37.24	13.22	17.86	10.51	29.20
OME	26.30	-	-	-	-	-
DME	4.43	30.28	17.35	17.35	-	-

The SynBio fuel type is represented by a little less than a third of the data points. The values are concentrated in a narrow range between 4.4 gCO<sub>2</sub>eq/MJ and 43.5 gCO<sub>2</sub>eq/MJ.

Environmental hotspots related to feedstock provision are the same for SynBio and Biofuels, as they only differ by the subsequent process chain. Even so, most analyzed SynBio FPPWs use biomass gasification to

produce syngas, which primarily utilizes lignocellulosic biomass as a feedstock. As this is a feedstock with comparatively low LUC emissions, this can partially explain their low GWP ranges compared to bio-based fuels. Only four of the analyzed SynBio pathways do not rely on lignocellulosic biomass. Those are shown in Table 7-8.

Table 7-8: SynBio fuels utilizing biomass other than lignocellulose.

Fuel Type	GWP [gCO <sub>2</sub> eq/MJ]	Feedstock	Refinery Process	Source
DME	4,43	Biomass (unspecified)	BTL	[121]
Methanol	5,25	Biomass (unspecified)	BTL	[121]
DME	29,86	Maize	GTL	[122]
Methanol	30,28	Maize	GTL	[122]

LUC impacts from starch rich biomass (maize) production are still way lower than for oil biomass. Biogas leakage from anaerobic digestion leads to additional GWP [122]. The unspecified biomass from [121] does not lead to emissions from LUC.

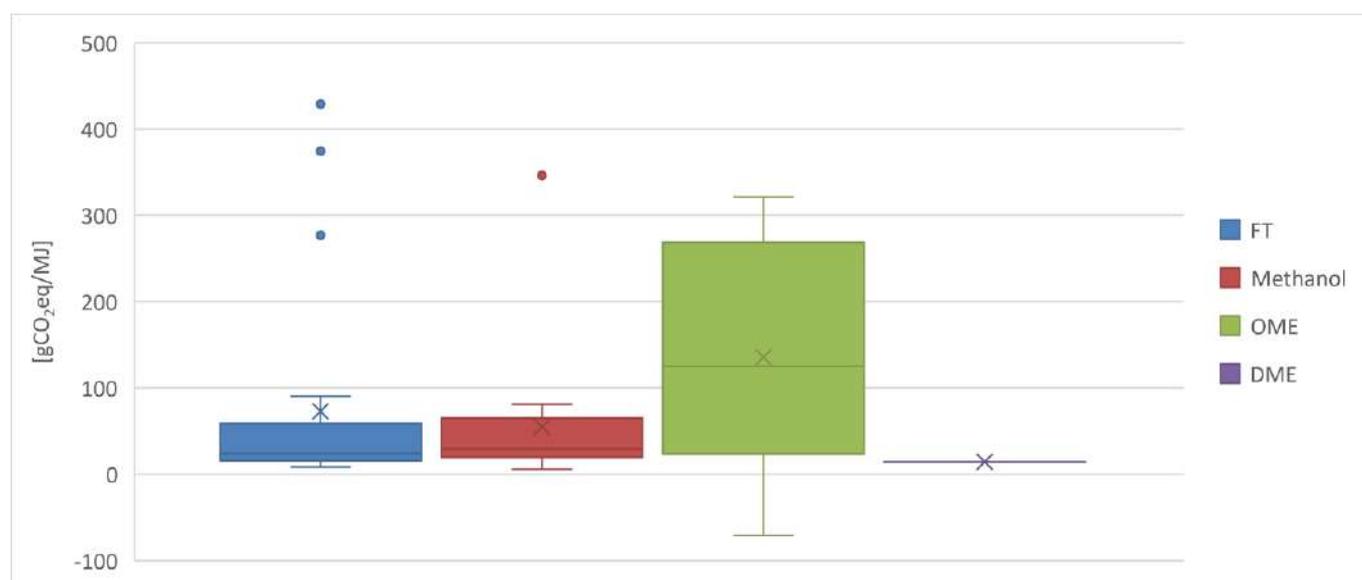


Figure 7-5: WTT GWP results for SynNoBio fuels. Number of data points N=50 (FT N=23; Methanol N=18; OME N=8; DME N=1).

Table 7-9: Overview of WTT GWP results for SynNoBio fuels.

Synthesis process	Min Value [gCO <sub>2</sub> eq/MJ]	Max Value [gCO <sub>2</sub> eq/MJ]	Median [gCO <sub>2</sub> eq/MJ]	Mean Value [gCO <sub>2</sub> eq/MJ]	Q1 [gCO <sub>2</sub> eq/MJ]	Q3 [gCO <sub>2</sub> eq/MJ]
FT	8.60	429.00	23.99	72.98	15.84	58.70
Methanol	6.00	346.42	29.42	54.61	19.37	64.97
OME	-70.82	321.10	125.08	135.50	23.62	268.46
DME	14.29	-	-	-	-	-

SynNoBio fuels make up the biggest part of the SynFuel dataset. Water electrolysis and CC are both energy-intensive, making the GWP of SynNoBio fuels very sensitive to the carbon intensity of the used energy mix. The outliers seen in Figure 7-5: are depicted in Table 7-10. All those pathways use energy with comparatively high carbon intensity.

Table 7-10: Outliers of the synthetic fuel's classification. In the region Germany (RE) the consumption of an electricity mix consisting of only renewable energy is assumed.

Fuel Name	WTT GWP [gCO <sub>2</sub> eq/MJ]	Region (Electricity Mix)	Process	Source
E-Diesel	429	Saudi Arabia	FT Synthesis	[123]
FT Fuel	374.34	Germany	FT Synthesis	[62]
E-Methanol	346.42	Germany	Methanol Synthesis	[62]
E-OME	321.09	Germany	PtL	[125]
Fossil-Syn-Gasoline	281.38	South Africa	FT Synthesis	Ecoinvent 3.7.1
E-Diesel	277	Germany	FT Synthesis	[123]
E-OME	272.99	Germany	PtL	[125]
E-OME	254.85	Germany	PtL	[125]
Ethanol	233.18	South Africa	FT Synthesis	Ecoinvent 3.7.1
Fossil-Syn-Methanol	189.28	South Africa	FT Synthesis	Ecoinvent 3.7.1
E-OME	164.48	Germany	PtL	[125]
Fossil-Syn-Diesel	155.65	South Africa	FT Synthesis	Ecoinvent 3.7.1
E-OME	-70.82	Germany (RE)	PtL	[125]

The GWP values from [123, 125, 62] are all attributable to a high carbon intensity electricity mix. A look at the countries, in which the production scenarios take place, supports this argument. In [123] it is stated that the Saudi Arabian energy mix is almost exclusively produced from fossil sources. German energy production also relies on fossil sources to a great degree [125, 62]. The lowest GWP Synfuel production scenario is an OME<sub>3-5</sub> pathway. The production process is (assumed to be?) fed by renewable energy. The CO<sub>2</sub> for fuel production is sourced from ammonia coproduction and crediting is applied which explains the negative WTT value [125].

### Individual process steps considerations

Among the various pathways for synthetic fuel production, the GWP range of approximately 500 gCO<sub>2</sub>eq/MJ was exceptionally wide. To determine possible hotspots of production pathways, the impacts of the individual process units are analyzed. Exact values about the impact of process units on the total carbon intensity of a synthetic fuel are scarce, however, the UBA [62] provided detailed information about every necessary step in synthetic fuel production chains. Therefore, the following sections focus mainly on the data found in this study. Whenever possible, values found elsewhere in the literature are added for comparison.

### Construction and Operation of the Fuel Production Plant

The synthesis plant itself was found to have only a minor effect. For FT synthesis plants the construction and operation of the plant, excluding all electric and thermal energy for hydrogen production and CO<sub>2</sub> provision, sums up to around 2 gCO<sub>2</sub>eq/MJ of produced FT fuels. The construction and operation of methanol plants account for approximately 4 gCO<sub>2</sub>eq/MJ of produced methanol. For construction and decommissioning of the synthesis plant 0.5-0.6 gCO<sub>2</sub>eq/MJ are reported [126]. Hence, it can be assumed that the major share of GWP influence of the plant on fuel production is due to plant operation. Obviously, the lower the total GWP of the production process the higher is the influence of plant construction, maintenance, and operation since it remains constant for every pathway. The main factor to influence the GWP of fuel is first and foremost the electrolyzer unit, followed by the type of carbon source.

## Electrolysis Unit

Three technologies are currently available to produce hydrogen from water, AEL, PEMEL, and SOEL. The efficiencies of electrolyzer stacks are expressed in relation to the LHV of hydrogen and are defined as

$$\eta_{LHV} = \frac{\dot{V}_{H_2} \cdot LHV_{H_2}}{P_{el}}$$

where  $V_{H_2}$  is the volume flow of hydrogen in  $Nm^3/h$ ,  $LHV_{H_2}$  is the LHV of hydrogen ( $3.0 \text{ kWh}/Nm^3$ ), and  $P_{el}$  is the electric energy consumed in kW. To describe the efficiency of electrolyzer systems, in addition to the energy demand of the stack, also energy demands for auxiliary units and heat supply must be considered. In general, the efficiency of the electrolysis system increases with decreasing current density and increasing temperature.

Commercial AEL electrolysis systems show rated efficiencies of 51-67 %<sub>LHV</sub> and specific system energy consumptions of  $5.0\text{-}5.9 \text{ kWh}/Nm^3$ . The specific energy consumption of AEL shows the tendency to decrease with increasing module capacity, since auxiliary system components operate more efficiently in larger modules. The lifetime of AEL systems is generally in the region of 55,000-120,000 hours.

PEMEL systems offer efficiencies ( $\eta_{LHV} = 46\text{-}67 \%$ ) and energy consumptions ( $5.0\text{-}6.5 \text{ kWh}/Nm^3$ ) in the same range. The lifetime of PEMEL systems is in the range of 60,000-100,000 hours. However, much higher current densities of up to  $2.0 \text{ A}/cm^2$  can be reached with PEMEL compared to  $0.45 \text{ A}/cm^2$  with AEL, resulting in higher hydrogen yields per cell area.

Most SOEL cells are operated at up to  $1.0 \text{ A}/cm^2$  with close to 100 % efficiencies based on LHV when operated at thermoneutral voltage. Using heat integration system efficiencies in the range of 76-81 %<sub>LHV</sub> has been reported. The specific energy demand for SOEL systems is reported in the range of  $3.7\text{-}3.9 \text{ kWh}/Nm^3$ . Data on the lifetime of SOEL systems, however, is tainted with a high degree of uncertainty due to the pre-commercial status of SOEL. In the current state of development lifetimes in the region of 10,000 hours seem realistic.

## Construction and Operation of the Electrolyzer Unit

The GWP for the construction and operation of the hydrogen production unit itself, excluding electric energy demand for the electrolysis, differs between the three available technologies. The carbon intensity of an AEL hydrogen plant is reportedly the lowest in the range of  $0.4\text{-}0.5 \text{ gCO}_2eq/MJ$  of produced fuel for both FT and methanol production pathways. The high temperature SOEL, however, accounts for almost  $3 \text{ gCO}_2eq/MJ$  of produced FT fuel, due to the limited lifetime of current SOEL applications. The construction and operation of PEMEL plants are responsible for approximately  $1.2\text{-}1.3 \text{ gCO}_2eq/MJ$  fuel. The higher GWP of PEMEL compared to AEL is likely due to the shorter lifetime of the plant. Additionally, PEMEL systems are often realized on a smaller scale with lower hydrogen production capacity than AEL plants, which of course increases the impact of construction and operation of the plant on the overall fuel GWP [127].

## Energy Source of the Electrolyzer Unit

In contrast to the relatively small contribution of the electrolysis plant construction and operation to the GWP of a fuel production process, the energy needed for water splitting is a major influence in most production pathways. Both the methanol and the FT production pathway with the highest overall GWP reported in the UBA [62] use the electricity mix of Germany in the year 2015 to produce fuel from flue gases and hydrogen. Of the total GWP of methanol ( $346 \text{ gCO}_2eq/MJ$ ) produced with this pathway,  $335 \text{ gCO}_2eq/MJ$  account for the energy demand for AEL hydrogen production. Of the total GWP for FT fuels ( $374 \text{ gCO}_2eq/MJ$ ) the energy needed for water electrolysis is responsible for  $367 \text{ gCO}_2eq/MJ$ . This is

of course due to the high share of fossil energy carriers in the 2015 electricity mix leading to a GWP of 527 gCO<sub>2</sub>eq/kWh [128]. Hank et al. [125] reported a GWP for the electrolysis of water using a PEMEL system of 170 gCO<sub>2</sub>eq/MJ for an OME production chain, assuming an electricity mix of 60 % 2018 German grid electricity plus 40 % renewable energy based on wind and photovoltaic plants. In 2018, the German electricity mix showed a carbon intensity of 471 gCO<sub>2</sub>eq/kWh [128]. The change of the electricity source from the 2015 grid mix to onshore wind power in the above described UBA pathways for methanol and FT fuel production drastically decreases the GWPs to 20 gCO<sub>2</sub>eq/MJ and 16 gCO<sub>2</sub>eq/MJ, respectively. Both UBA [62] and Hank et al. [125] report hydropower electricity as the best option for hydrogen generation via water splitting. Using hydropower in AEL applications decreases the GWP of the energy demand of the electrolysis to 1.2-1.7 gCO<sub>2</sub>eq/MJ fuel. Even a share of 60 % hydropower in a mix with 40 % of other renewable energy sources lowers the GWP of electrolysis to 11 gCO<sub>2</sub>eq/MJ OME in OME production pathways using PEMEL.

### CO<sub>2</sub> Source

The carbon sources for synthetic fuels can be distinguished into point source capture and DAC for PtL production pathways. For BtL and PBtL production pathways, biomass serves as the carbon source. The GWP impacts of the carbon sources for synthetic fuels on the overall GWPs of fuels are much smaller than the electricity source for water electrolysis. Point sources and DAC approaches vary in their contribution to the total GWP of the produced fuel, due to their different energy and material demands. Von der Assen et al. [130] presented a study assessing the GWP of several CO<sub>2</sub> sources per captured ton of CO<sub>2</sub>, considering the electric as well as the thermal energy demand to capture CO<sub>2</sub> from the respective source, and the transportation of CO<sub>2</sub> to the utilization plants. The most favorable GWP (0.06 tCO<sub>2</sub>eq/tCO<sub>2</sub> captured) can be achieved by capturing CO<sub>2</sub> from almost pure sources such as ammonia, natural gas processing, or biomass fermentation. Capturing CO<sub>2</sub> from coal-fired power plants and industries such as iron and steel mills, the GWP per captured ton CO<sub>2</sub> is in the range of 0.17-0.22 tCO<sub>2</sub>eq. Carbon capture in cement production has a GWP of 0.37 tCO<sub>2</sub>eq/tCO<sub>2</sub> captured. DAC units are generally located in proximity to CO<sub>2</sub> utilization plants and therefore the GWP of CO<sub>2</sub> transport is negligible. However, due to the high energy intensity the GWP for DAC approaches is reported to be as high as 0.46 tCO<sub>2</sub>eq/tCO<sub>2</sub> captured. Yet, von der Assen et al. [2] assumed the use of natural gas to meet the thermal energy demand of the DAC units. Using waste heat from industrial plants to provide thermal energy has a beneficial effect and would most certainly decrease the GWP of DAC.

### Carbon Capture from Point Sources

CO<sub>2</sub> from point sources can be captured by various different technologies, as mentioned in chapter 0. The technologies differ in the demands of both thermal as well as electrical energy. Amine scrubbing is often used in industrial facilities such as coal- or natural gas-fired power plants to separate and capture CO<sub>2</sub> from the flue gas streams. The majority of the energy demand is thermal energy for the regeneration of the amine sorbent in a stripper column. Per ton captured CO<sub>2</sub> the heat demand for amine scrubbing using monoethanolamine is in the range of 890-1520 kWh<sub>th</sub> [62, 131]. With advanced amine absorbent solution, the heat requirement for regeneration can be reduced to 720 kWh<sub>th</sub>/tCO<sub>2</sub> [131]. The electrical energy demand to operate fans, pumps, and gas compression systems in chemical absorption technologies is in the range of 220-460 kWh<sub>el</sub>/tCO<sub>2</sub> [62, 74, 131]. Physical absorption processes, such as the Rectisol process and the Selexol process use pressure swings to regenerate the solvents for CO<sub>2</sub> separation. Therefore, the energy demand is covered by electricity in the range of 300-600 kWh<sub>el</sub>/tCO<sub>2</sub> [62].

As mentioned in chapter 6.3.5.2.2, the off gas from cement production plants and coal-fired power generation plants has CO<sub>2</sub> concentrations of 10-33 % and 10-12 %, respectively. The influence on the total fuel GWP of the production and operation of the capture unit, excluding the thermal and electrical energy

necessary for CO<sub>2</sub> provision, is miniscule and therefore negligible. The energy needed to provide CO<sub>2</sub> for utilization depends on the type of CC technology. The UBA report [62] assumes an amine scrubbing approach to capture CO<sub>2</sub> from coal-fired power plants and states GWP values of 2.7 gCO<sub>2</sub>eq/MJ FT fuel and 3.1 gCO<sub>2</sub>eq/MJ methanol respectively. The energy demand for amine scrubbing is less dependent on electrical energy but heavily on thermal energy which can be provided by waste heat from industrial processes. For the CO<sub>2</sub> separation from cement production off gas streams the energetically beneficial Selexol process was assumed resulting into a lower GWP in the range of 0.5-2.0 gCO<sub>2</sub>eq/MJ methanol. The Selexol process, however, is strongly dependent on electrical energy and therefore relies on the electrical energy source. The UBA [62] investigated several pathways with different electricity sources using cement production off gases as CO<sub>2</sub> source. The use of concentrated solar power in Saudi Arabia resulted into the lowest GWP the Selexol process (0.5 gCO<sub>2</sub>eq/MJ methanol), PV in Germany was less attractive with a GWP of 2.0 gCO<sub>2</sub>eq/MJ methanol. For FT fuels no GWP data regarding the Selexol process could be found. However, these relatively small GWP values for CO<sub>2</sub> sourcing from cement production plants and coal-fired power plants are the result of fully allocating the fossil CO<sub>2</sub> emissions of the processes to the final products cement and electrical energy, and not the fuel production processes. If the CO<sub>2</sub> emissions from fossil sources are considered in the FPPWs, a GWP of 77 gCO<sub>2</sub>eq/MJ fuel must be added to the GWP of the final fuel.

The fuel pathways with the lowest overall GWP reported by UBA [62] use CO<sub>2</sub> from anaerobe digestion of biomass. The digestion of biomass produces mixtures of mainly methane and CO<sub>2</sub> with a CO<sub>2</sub> content of 40-45 %. Since biomethane is the target product of the process and the produced CO<sub>2</sub> is usually released in the atmosphere, it is regarded as waste and all energetic demands for separation are allocated to CH<sub>4</sub>. Hank et al. [125] reported a GWP value 49 gCO<sub>2</sub>eq/MJ OME for CO<sub>2</sub> sourcing from biomethane in an OME production pathway. However, this value was subtracted from the overall GWP of the fuel, since this GWP was also fully allocated to the biomethane and not the FPPW.

### Direct Air Capture

Compared to concentrated point sources the concentration of CO<sub>2</sub> in ambient air is extremely low. The energy demand of DAC approaches is therefore heavily dominated by the thermal component for the regeneration of the sorbent. The ultra-low concentrations of CO<sub>2</sub> in ambient air compared to gas streams from point sources necessitate sorbents with a strong binding chemistry towards CO<sub>2</sub>, leading to a high thermal energy demand for producing high-purity CO<sub>2</sub> from the air [132]. Values for the thermal energy demand of DAC systems found in literature are not consistent and scattered over a wide range, but generally Low temperature DAC (LT-DAC) units are considered to require less thermal energy than HT-DAC units due to the lower regeneration temperatures.

The UBA [62] reports a thermal energy demand of 1700-2200 kWh<sub>th</sub>/tCO<sub>2</sub> using LT-DAC. According to Fasihi et al. [78], the thermal energy demand to capture one ton of CO<sub>2</sub> is in the range of 1500-2000 kWh<sub>th</sub> and 1170-1410 kWh<sub>th</sub> for amine based and amine polymer-based LT-DAC systems, respectively. Other sources [132, 133] report thermal energy requirements in the range of 800-1530 kWh<sub>th</sub>/tCO<sub>2</sub>. LT-DAC systems generally use low grade waste heat from industrial plants to cover the thermal energy needs. HT-DAC systems use temperatures of up to 900 °C to regenerate the solvent resulting in higher thermal energy demands, with reported values in the ranges of 1420-2780 kWh<sub>th</sub>/tCO<sub>2</sub> [78], 1460-2250 kWh<sub>th</sub>/tCO<sub>2</sub> [133], and 2140-2970 kWh<sub>th</sub>/tCO<sub>2</sub> [132]. The thermal energy for the regeneration of the sorbent material in HT-DAC processes is often provided the burning of natural gas. However, due to the burden of 0.5 tons CO<sub>2</sub> being released from natural gas per ton of captured CO<sub>2</sub>, a fully electrified heating system powered by renewable energy seems the most promising solution for this technology. Apart from thermal energy, DAC systems require electricity to operate fans, pumps, and control systems. Additionally, HT-DAC units need electrical energy to spray the aqueous solution in the air contactor and

move the solutions between the individual reaction loops [78]. The UBA [62] reports a comparatively high electrical energy demand for LT-DAC systems of 700 kWh<sub>el</sub>/tCO<sub>2</sub>, whereas 150-300 kWh<sub>el</sub>/tCO<sub>2</sub> have been reported elsewhere [78, 132, 133]. These sources also report electrical energy demands for HT-DAC systems in the range of 250-760 kWh/tCO<sub>2</sub>.

According to the UBA report [62], the construction and operation of the DAC units, excluding thermal and electrical energy necessary for CO<sub>2</sub> provision, sums up to about 4.5-5 gCO<sub>2</sub>eq/MJ of fuel for both FT and methanol production pathways. This highest GWP of all investigated carbon provision pathways is not surprising, since the ultra-low concentration of CO<sub>2</sub> in air compared to point sources demands large quantities of materials and chemicals per ton of captured CO<sub>2</sub> [133]. For the FT pathways using DAC with the lowest overall GWP ranging from 17-24 gCO<sub>2</sub>eq/MJ of produced FT fuel reported by UBA [62], the construction and operation of the DAC unit itself is therefore responsible for about 18-25 % of the carbon intensity of the fuel. The share of the DAC unit of the overall GWP of DAC supplied methanol pathways with low carbon intensity (22-27 gCO<sub>2</sub>eq/MJ of produced methanol) is in the range of 18-23 %. The energy intensive DAC approach can utilize waste heat from exothermic processes such as methanol or FT synthesis, but not all of the required energy for CO<sub>2</sub> provision can be covered by waste heat with current DAC technologies. Therefore, the GWP of the thermal and electrical energy demand of DAC depends in part on the carbon intensity of the electricity source. The UBA report [62] states values for 7 gCO<sub>2</sub>eq/MJ FT fuel and 18 gCO<sub>2</sub>eq/MJ methanol for the energy needed for DAC if photovoltaic in Germany is assumed as energy source. Switching to offshore wind power, these values can be reduced to 1 gCO<sub>2</sub>eq/MJ FT fuel and 2.5 gCO<sub>2</sub>eq/MJ methanol, respectively, due to the higher GWP of PV compared to wind power. This is in accordance with the numbers stated by Liu et al. [126], who report a GWP of 1.4 gCO<sub>2</sub>eq/MJ FT fuel for the operation of an HT-DAC unit using electrically heated calciner in British Columbia, where the hydro-dominated grid mix has a low carbon intensity of about 13 gCO<sub>2</sub>eq/kWh. Hank et al. [125] report comparable results for a LT-DAC unit using an electricity mix of 60 % hydropower plus 40 % renewable energy based on wind and photovoltaic plants for the electrical energy demand and the exhaust heat of an OME synthesis plant to partly cover the thermal energy demand. The remaining thermal demand was covered by additional available exhaust heat, which resulted in a total GWP of CO<sub>2</sub> sourcing of 16 gCO<sub>2</sub>eq/MJ OME. However, if no additional exhaust heat is available and natural gas is used to provide the required thermal energy, the GWP of CO<sub>2</sub> sourcing increases to 65 gCO<sub>2</sub>eq/MJ OME. In an OME production pathway using the above energy mix, the use of natural gas for thermal energy provision for the DAC approach would therefore account for 76 % of the overall GWP of 86 gCO<sub>2</sub>eq/MJ OME.

### Biomass

A possible carbon source for FT fuel and methanol production is also the gasification of biomass. Here, it can be distinguished between biomass especially planted for energy use, such as short rotation forestry (SRF), and forestry residues which are considered as waste. For biomass waste, no cultivation emissions are considered, only the impacts of collection and pre-treatment. According to UBA [62] and O'Connell [134] the growing, harvesting, chipping and transport of SRF are responsible for the major share of GWP in BtL FPPWs in the range of 9.8-12.1 gCO<sub>2</sub>eq/MJ FT fuel. Using forest residues this GWP can be reduced to 1.5-5.4 gCO<sub>2</sub>eq/MJ FT fuel. The process of gasification and fuel synthesis emits 0.6 gCO<sub>2</sub>eq/MJ fuel and only plays a minor part in the overall fuel GWP.

## 7.4 Gaseous Fuels

The difference in the WTT GWP ranges for gaseous fuel production can be attributed to similar hotspots as in liquid fuel production. The carbon intensity of the used electricity mix is of very high significance for synthetic pathways. This argument is further supported by a Monte Carlo sensitivity analysis performed in [3], which identified the energy mix as one of the most impactful parameters of the model. Carbon emissions from bio-based gas production is again affected by LUC to a high degree. As oily biomass is not used in any of the pathways, the extent to which LUC affects the results is smaller than for liquid bio-based fuels. Biogas leakage from anaerobic digestion is of significant impact as well. The NG FPPWs have relatively low GWP, which can mostly be attributed to the low effort needed to extract it.

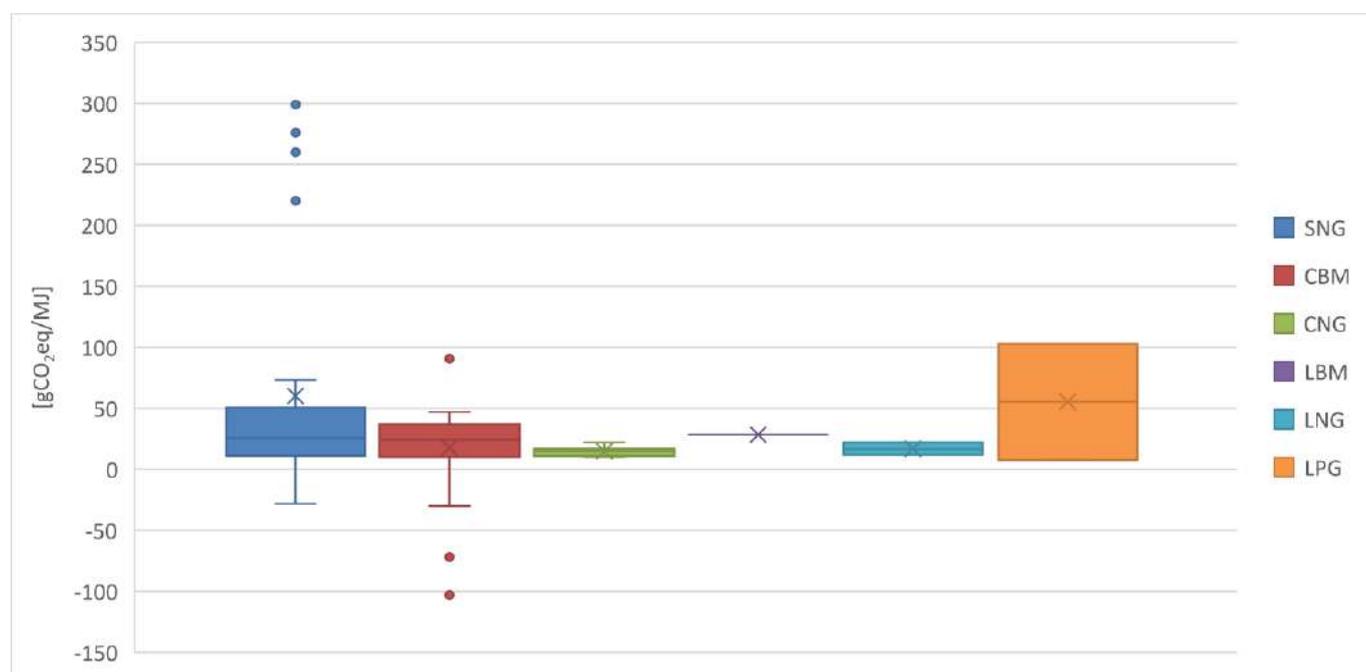


Figure 7-6: WTT GWP results for gaseous fuels. Number of data points N=67 (SNG N=32; CBM N=23; CNG N=6; LBM N=1; LNG N=3; LPG N=2).

Table 7-11: Overview of WTT GWP results for gaseous fuels.

Fuel Type	Min Value [gCO <sub>2</sub> eq/MJ]	Max Value [gCO <sub>2</sub> eq/MJ]	Median [gCO <sub>2</sub> eq/MJ]	Mean Value [gCO <sub>2</sub> eq/MJ]	Q1 [gCO <sub>2</sub> eq/MJ]	Q3 [gCO <sub>2</sub> eq/MJ]
SNG	-28.24	301.97	25.54	60.06	11.04	50.70
CBM	-103.00	90.55	24.20	17.55	10.10	37.00
CNG	10.00	22.00	15.00	14.71	10.88	16.83
LBM	28.41	-	-	-	-	-
LNG	11.93	22.00	16.60	16.84	11.93	22.00
LPG	7.80	102.73	55.27	55.27	-	-

Table 7-12: Outliers of the gaseous fuel classification.

Fuel Name	WTT GWP [gCO <sub>2</sub> eq/MJ]	Region (Electricity Mix)	Process	Source
SNG	301.97	Germany	Methanation	[62]
SNG	299	Europe	Methanation	[135]
SNG	276	Europe	Methanation	[135]
SNG	260	Austria	Methanation	[136]
SNG	220	Austria	Methanation	[136]
LPG	102.73	South Africa	FT Synthesis	Ecoinvent 3.7.1
CBM	90.55	Germany	Anaerobic Digestion	[3]
SNG	73.08	South Africa	FT Synthesis	Ecoinvent 3.7.1
SNG	-27.86	Germany	Anaerobic Digestion	[3]
SNG	-28.23	Germany	Methanation	[3]
CBM	-30.1	Europe	Biogas Upgrading	[10]
CBM	-71.8	Canada	Methanation	[137]
CBM	-103	Europe	Anaerobic Digestion	[119]

The studies [135, 136, 62] are attributing their outliers towards the upper range limit consistently to the high GWP of the electricity mix utilized in the fuel production process, as high quantities of electric energy are needed for the production of hydrogen. According to [135] it is not sufficient to use waste CO<sub>2</sub> to offset the impacts from the utilization of a high GWP electricity mix.

Analyzing the GWP values collected from [119, 137, 10], it is evident that lower end outliers are due to the lacking consideration of LUC in the impact assessment. In combination with crediting, this leads to very low carbon footprints. In the respective FPPWs the utilization of manure leads to carbon credits since the otherwise emitted methane from anaerobic digestion is avoided. The values collected from [3] were calculated in a similar way, the reuse of waste CO<sub>2</sub> for the methanation process results in carbon crediting. Coal gasification leads to comparatively speaking high WTT carbon footprints due to the feedstocks high carbon content and low hydrogen content.

The fuels are either transported in a compressed gaseous or liquified state. Impacts from gas transport are dependent on the state of the transported gas. LNG is much denser than CNG, but the liquification leads to additional energy demand. The same amount of energy can be transported in a smaller vessel in the case of LNG. On the other hand, less energy is required to compress NG and it can be transported via highly energy efficient pipelines over long distances. Pipelines however often lead to problems with diffusion leakage, where gas escapes into the atmosphere and contributes to global warming.

## 7.5 Projections

In this section, data points for the time frame of 2030 to 2050 are analyzed to show a possible trend in development of GWP values for alternative fuels in the future. GWP values for synthetic fuels are only available for 2050 and most of the values are provided by [62] (44/48; 91.6 %). Gaseous fuel projections are exclusively sourced from this report. Data on bio-based fuels is sourced from [119]. The chosen timeframe for projections in [119] is 2030 which is adapted for bio-based fuel results in this section.

### Bio-based fuels

[119] draws the conclusion that no major decreases in the GWP of bio-based fuel production can be expected by 2030 in Europe. This is because most of the fuels are still produced from biomass that rivals other product use, especially food. As seen in Figure 7-7 projected median GWP reduction amounts to

about 22 % but the IQR increases by 11 %. Which leads to the conclusion that no significant changes to the feedstock will be made until 2030. Improvements to the GWP could be achieved by switching to waste- and residue-based feedstocks, or by further developing rather new technologies like DTL.

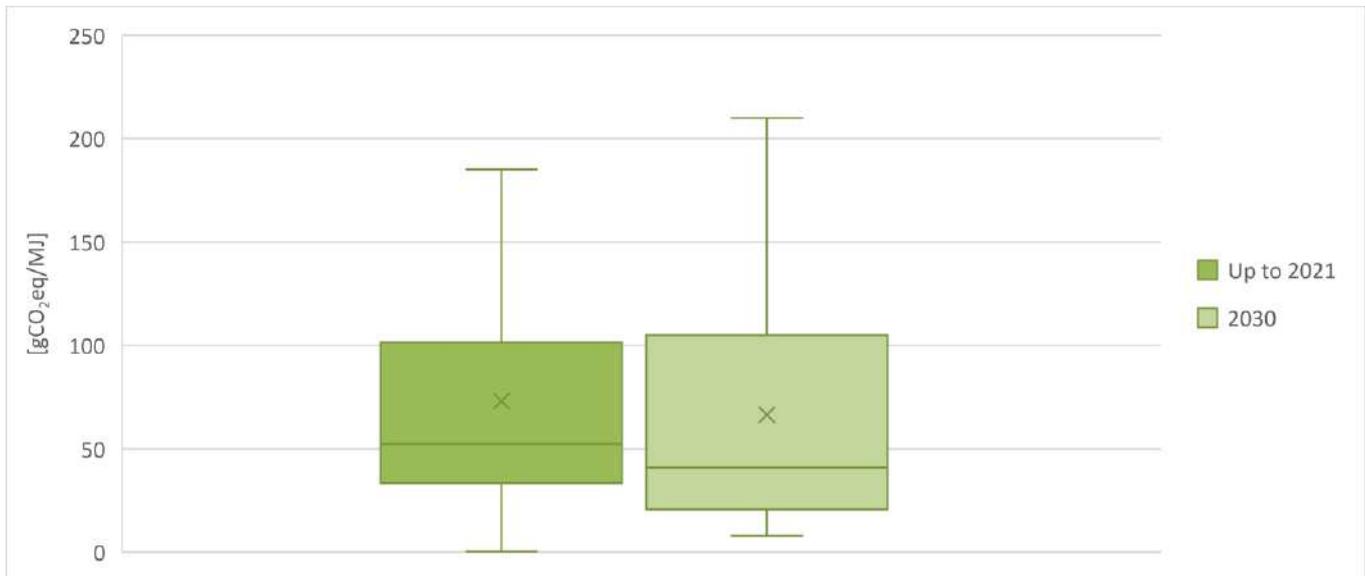


Figure 7-7: current and projected WTT GWP results for bio-based fuels.

Table 7-13: Selection of statistical parameters of bio-based fuels for the time frame of up to 2021 and 2030.

Time Horizon	Min Value [gCO <sub>2</sub> eq/MJ]	Max Value [gCO <sub>2</sub> eq/MJ]	Median [gCO <sub>2</sub> eq/MJ]	Mean Value [gCO <sub>2</sub> eq/MJ]	Q1 [gCO <sub>2</sub> eq/MJ]	Q3 [gCO <sub>2</sub> eq/MJ]
Up to 2021	0.40	267.00	52.40	73.12	33.43	101.50
2030	8.00	210.00	41.00	66.44	20.80	105.00

### Synthetic fuels

Figure 7-7 shows a steep decline of about 55 % in median WTT GWPs for synthetic fuels until 2050. [62] attributes this development mainly to the reduced carbon intensity of the electricity mix for hydrogen production. [62] also predicts an about 13 % decrease in cumulated energy (MJ/MJ fuel) demand until 2050. Some GWP reduction potential is also attributed to improved production processes for building materials used in facility construction. [125] predicts only a minor decrease in GWP from improvements to electrolysis hardware but agrees with [62] on the role of the electricity mix in the emission trajectory.

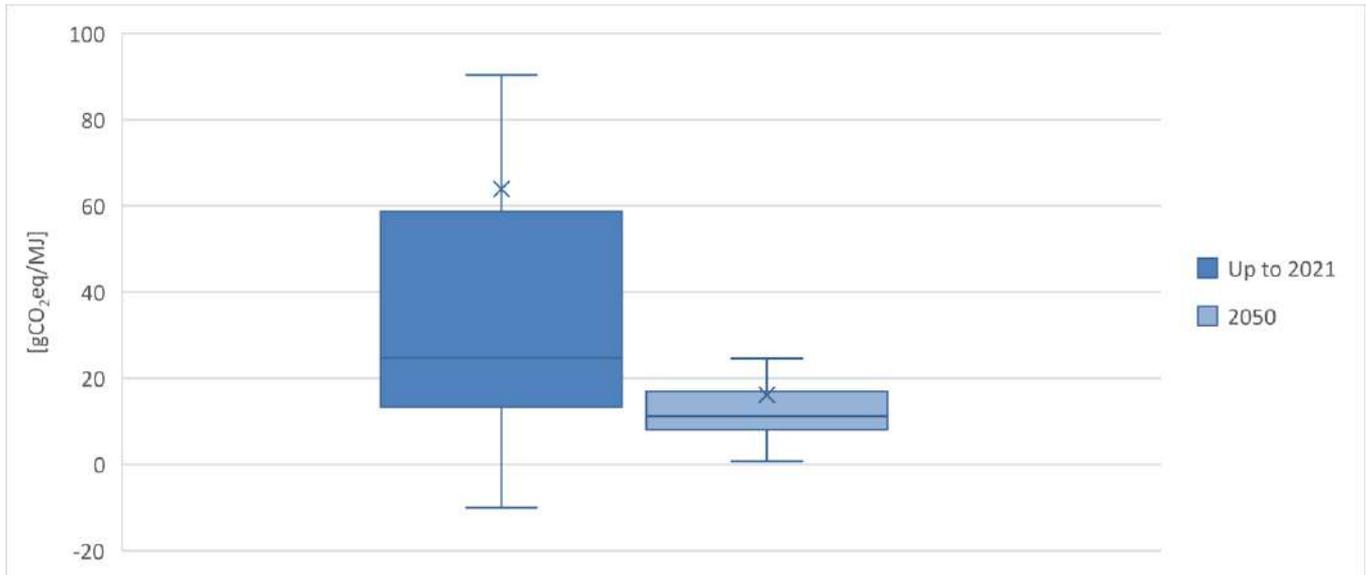


Figure 7-8: current and projected WTT GWP results for synthetic fuels

Table 7-14: Selection of statistical parameters of synthetic fuels for the time frame of up to 2021 and 2050.

Time Horizon	Min Value [gCO <sub>2</sub> eq/MJ]	Max Value [gCO <sub>2</sub> eq/MJ]	Median [gCO <sub>2</sub> eq/MJ]	Mean Value [gCO <sub>2</sub> eq/MJ]	Q1 [gCO <sub>2</sub> eq/MJ]	Q3 [gCO <sub>2</sub> eq/MJ]
Up to 2021	-70.82	429.00	24.73	63.91	13.30	58.70
2050	-29.51	112.24	11.19	16.12	8.08	16.97

### Gaseous fuels

The whole dataset is sourced from the report [62]. The projected data includes four biomethane and twelve SNG pathways. While biomethane production is predicted to only achieve minor GWP reductions as it already uses waste biomass in this case, SNG pathways are responsible for the steep decline of about 43 % in median WTT carbon footprints shown in Figure 7-8. This decline is, again, mostly attributed to reductions in the carbon intensity of electricity.

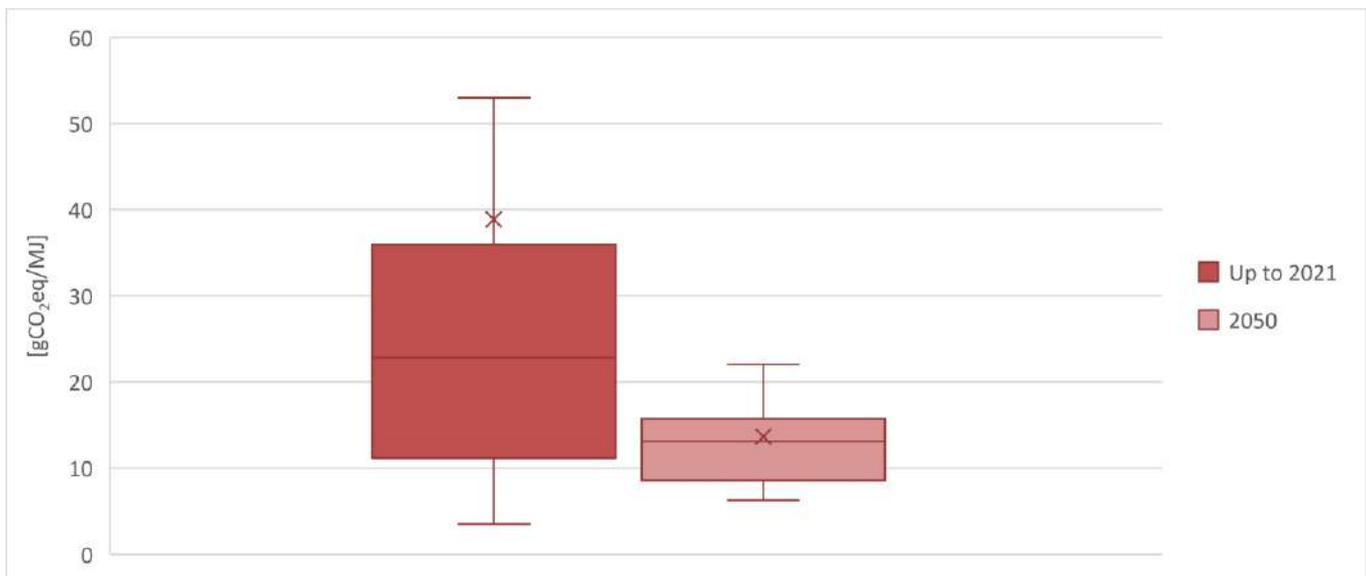


Figure 7-9: current and projected WTT GWP results for gaseous fuels.

Table 7-15: Selection of statistical parameters of gaseous fuels for the time frame of up to 2021 and 2050.

Time Horizon	Min Value [gCO <sub>2</sub> eq/MJ]	Max Value [gCO <sub>2</sub> eq/MJ]	Median [gCO <sub>2</sub> eq/MJ]	Mean Value [gCO <sub>2</sub> eq/MJ]	Q1 [gCO <sub>2</sub> eq/MJ]	Q3 [gCO <sub>2</sub> eq/MJ]
Up to 2021	-103.00	301.97	22.80	38.86	11.17	35.93
2050	6.28	30.85	13.10	13.65	8.59	15.72

Summarizing, most pathways that need large amounts of electric energy, have great GWP reduction potential through the decarbonization of electricity. The reduction potential from improved process technology and sustainable facility construction cannot be assessed with a similar degree of certainty. Bio-based FPPWs have the greatest reduction potential in the change from traditional, product rivaling, feedstocks to advanced feedstocks.

## 7.6 Midpoint Indicator Results for Fuel Production

This chapter's focus is on findings for various midpoint indicators related to fuel production. Since climate change related impacts have already been elaborated in detail, GWP will not be mentioned here.

As described in section 4.6, the representation of midpoint indicators in literature concerning their units and the corresponding characterization factors is rather inconsistent. In addition, many of the reviewed studies don't expand their analysis beyond climate change related impacts. Therefore, this section will only include tendencies and qualitative findings for some midpoint indicators and provide an overview of possible environmental hotspots found in literature. Taking these factors into account, the results presented in this section come with a higher degree of uncertainty than the GWP related results as they rely on a much smaller sample size of studies.

Table 7-16: Overview of some median midpoint indicators from [62], the cursive values are the min and max values for the corresponding datasets

	Acidification [mgSO <sub>2</sub> eq/MJ]	Eutrophication [mgPO <sub>4</sub> <sup>3-</sup> eq/MJ]	Water Depletion [mL/MJ]	Cumulated Energy Demand [KJ/MJ]	Feedstock	N
<b>Fischer Tropsch fuel</b>	177 <i>131-6205</i>	77 <i>27-209</i>	326 <i>154-3365</i>	2556 <i>2198-6593</i>	non-biomass	17
<b>Fischer Tropsch fuel</b>	242 <i>43-645</i>	53 <i>10-154</i>	5169 <i>340-17262</i>	2488 <i>2374-3311</i>	biomass	7
<b>Methanol</b>	261 <i>154-5800</i>	97 <i>39-234</i>	336 <i>193-5119</i>	2802 <i>2145-6548</i>	non-biomass	14
<b>Methanol</b>	192 <i>84-706</i>	57 <i>23-148</i>	2887 <i>155-16628</i>	2336 <i>2043-3468</i>	biomass	6

The acidification potential (AP) of almost all alternative fuel pathways is higher than the fossil reference of 74 mgSO<sub>2</sub>eq/MJ. Using geothermal energy to provide electricity for SynNoBio pathways results in AP values up to 80 times higher than the fossil reference due to the H<sub>2</sub>S emissions associated with geothermal energy. Also, the use of grid electricity with high content of fossil sources imparts high AP values due to sulfur oxide and nitrous oxides emissions related to the electricity production. Additionally, ammonia emissions from the use of cultivated biomass, fertilizers and nitrous oxides related to the use of diesel fuel for agricultural machinery effect the AP. Only pathways using electricity from wind power or waste biomass show lower AP values than the fossil reference. Projections on the median AP for synfuels are still 2.2 times higher than the fossil reference in 2050 [62, 10].



The fossil reference for the eutrophication potential (EP) is 21 gPO<sub>4</sub><sup>3-</sup>eq/MJ and almost all production pathways of alternative fuels exceed this threshold. Pathways having a massive impact on the EP of a fuel of 700-1,000 % use PV energy or electricity from current primarily fossil-based grid mixes. The production and disposal of PV panels as well as mining operations for coal provision are associated with nitrogen and phosphorous emissions. The use of fertilizers for the cultivation of biomass is associated with the leaching of nitrates and phosphates into the soil contributing to elevated EP values of the fuels. Pathways using waste biomass such as straw and forestry residues or hydropower, however, show EP values below the fossil reference. The median EP is projected to be 3.2 times higher than the fossil reference in 2050. Here, the provision of steel, copper, and aluminum for building power plants as well as ammonia emissions from biogenic feedstock cultivation are identified as main drivers for eutrophication [62, 10].

The cumulated energy demand (CED) of fossil fuels is 1.2 MJ/MJ. None of the pathways to produce alternative fuels shows CED values below the fossil reference. The CED for pathways using the current grid mix or PV electricity have CEDs about three times higher than the fossil reference. The main influences on CED are the electricity demand of the electrolyzer unit and the cultivation of biomass. The current median CED for synthetic fuels is 2.5 MJ/MJ, meaning only 40 % of the invested energy is stored in the fuel. The CED of synthetic fuels is projected to rise to 2 MJ/MJ in the year 2050 [62]. Predictions say that an increase in energy efficiency will play a minor role in comparison to decrease of carbon intensity in the electricity mix [125].

As seen in Table 7-16 biomass reliant synfuels tend to lead to high water depletion (WD) in comparison to non-biomass reliant synfuels, yet all pathways to produce alternative fuels show higher WD than the fossil reference of 67 mL/MJ. This originates from the water consumption during feedstock cultivation leading to extensive WD values of 27 000 % higher than that of the fossil reference for fuels based on cultivated biomass. Water depletion is projected to be 5.7 times higher than the fossil reference in 2050 [62].

Land occupation will be up to 6 800 times higher, with hotspots being the cultivation of biomass and the production of solar power plants [62].

The ozone depletion potential (ODP) of almost all alternative fuel production pathways is higher than the ODP of the fossil reference of 0.0064 mgCFC-11eq/MJ. Pathways utilizing concentrated solar power show ODP values almost 60 times higher than the fossil reference, as the production of liquid salts for thermal storage is associated with N<sub>2</sub>O emissions. For pathways using biomethane, the residue storage and the operation of the on-site biogas power plant are the main contributors to ozone depletion. Energy crops such as SRF carry an ODP burden stemming from the cultivation of biomass. The median value for synthetic fuel production in 2015 is ten times as high as the fossil reference, only decreasing to eight times the fossil reference in 2050. Pathways with ODP values lower than the fossil reference use waste biomass such as forestry residues or straw [62].

Finally, the generation of particulate matter > 10 µm (PM<sub>10</sub>) associated with the production of fossil fuels is 65 mg/MJ. Only biobased fuels and SynBio fuels produced from waste biomass show PM<sub>10</sub> values below the fossil reference. The main influence to the PM<sub>10</sub> generation is the electricity for water electrolysis from current grid mixes based on fossil energy carriers and PV, as well as the cultivation of biomass. The median value of PM<sub>10</sub> for 2015 scenarios as well as for 2050 scenarios is double the value of the fossil reference. [62].

## 7.7 System Boundaries in Examined LCAs

The choices on system boundaries define different scenarios and the level of detail of an LCA. The assignment of impacts to different life cycle-stages may have no influence on WTW results but contributes to the widespread distribution of WTT results. This assignment is quite homogenous in literature, apart

from the placement of crediting and LUC in the lifecycle. Other system boundary specifications such as cut-off criteria for waste treatment or implementation of transport related burdens were evaluated in the literature screening. The results were not adjusted to mitigate those differences, since this study's objective is not to assess the likelihood of scenarios but to present their peculiarities. All studies contain information on feedstock provision and refinery operation. Transport, distribution, and waste treatment are often depicted to a much lower grade of detail or even excluded.

## 7.8 Carbon Crediting

Crediting in LCAs refers to subtracting avoided impacts (in this case GWP expressed in gCO<sub>2</sub>eq/MJ) from the impact indicator results. This occurs mostly for CC or biogenic feedstock production. Crediting is not exclusive to those cases. Crediting is also used if waste is utilized that would have led to carbon emissions if it's disposed or if the system yields by-products that can offset consumption somewhere else. This can for instance be seen in [125].

In most LCA models that assess alternative FPPWs GWPs, some form of crediting is applied for the reuse of bound carbon. However, the exact execution varies. While some studies use these credits to offset the emissions from fuel combustion, others apply credits in the WTT phase, leading to often negative emission values for fuel production. This makes a huge difference in WTT results and can lead to limited comparability between studies. Some negative GWP values for fuel production can be seen in the results section of this study.

From a WTW viewpoint those two approaches might be equivalent, but it has a significant impact on the results if only parts of the life cycle are assessed. In most cases crediting is applied such that it mitigates the emissions from fuel combustion. This might not be true for some FPPWs since it is well possible that the final product contains only a percentage of the previously bound carbon.

In [3] system boundaries are chosen in a way that exaggerates benefits from crediting by cutting of waste treatment, letting bound carbon leave the system in a non-fuel form i.e. not accounting for its reemission. This leads to negative carbon footprints. SNG from demolition wood pellets reaches that way a WTT footprint of -480.7 gCO<sub>2</sub>eq/MJ and -402.8 gCO<sub>2</sub>eq/MJ from a WTW perspective (533.8 gCO<sub>2</sub>eq/MJ credited). Representing extreme outliers, those values were not taken into account for this study.

## 7.9 Land Use Change

Emissions from LUCs are difficult to evaluate since they heavily depend on the carbon binding capacity of the transformed land. [2] shows how severe the impacts of LUC can be and how much they change depending on different system choices. Taking the potential magnitude of LUC burdens into account, disregarding it in LCA models could lead to severe underestimation of carbon footprints, especially for bio-based fuels and SynBio Fuels. Guidelines for the calculation of LUC-related impacts can be found in annex VI of [138]. While DLUC can often be calculated directly, ILUC can only be approximated in most cases.

Not all fuel pathways that rely on biomass cause LUC, i.e., waste biomass. In the case of these bio-based fuels, they are often referred to as advanced or second-generation bio-based fuels. The classification for advanced bio-based fuels given in RED II is briefly shown in 6.2. In order to be considered LUC free, biomass has to be considered waste (i.e., feedstock production does not lead to other foregone products and does not occupy additional acreage).

Annex VIII of [138] gives an overview of estimated values for ILUC attributed to different biogenic feedstocks which are shown in Table 7-17.

Table 7-17: ILUC estimates by feedstock class after RED II

<b>Feedstock</b>	<b>ILUC mean value</b>	<b>Bandwith</b>
Cereals and other starch rich crops	12 gCO <sub>2</sub> /MJ	8-16 gCO <sub>2</sub> /MJ
Sugar rich crops	13 gCO <sub>2</sub> /MJ	4-17 gCO <sub>2</sub> /MJ
Oil crops	55 gCO <sub>2</sub> /MJ	33-66 gCO <sub>2</sub> /MJ

This evaluation shows the highest ILUC burden on oil-based bio-based fuels such as FAME and HVO, which is in line with the GWP results shown before.

The LUC contributing to the highest GWP values in 7.2 is many times higher than the average values given by the RED II. This is because the corresponding models use specific LUC scenarios including a large share of deforestation. [2] compares different methodological choices in LCA for different fuel pathways, showing that taking LUC into account, FAME and HVO are almost never fit to satisfy the RED II emission reduction threshold in any model. FAME production can satisfy the threshold if it uses waste oil. The burdens from LUC depend on the type of transformed land. Supplementary material to [2] even shows negative LUC emissions for oil palm fruit production (- 8.6 tCO<sub>2</sub>eq/ha/yr) in Indonesia if annual cropland is used, but it is assumed that 92.6 % of oil palm production expansion in Indonesia displaces natural forests which leads to much higher LUC burdens (15.5 tCO<sub>2</sub>eq/ha/yr). Soybean production is said to lead to even higher LUC emissions when displacing natural forests, but a higher percentage is produced on annual cropland. Using annual cropland for production might however lead to ILUC since foregone commodity production has to be accounted for.



## 8 CONCLUSION

Even though the LCA results from literature come with uncertainties, it is still possible to define ranges for GWP impacts and tendencies for other environmental impact indicators related to fuel production. LCA is still the most comprehensive way to evaluate midpoint indicators considering there is no clear standard for evaluating environmental impacts of fuels.

The WTT viewpoint contributes further to a lack of comparability and uncertainty since the attribution of system components to life cycle stages is not homogenous in literature. CLCAs are better suited for decision making, since they assess changes in demand and production as opposed to ALCAs which assess current average data [2] [10]. Yet almost all LCA studies that were found in the literature screening are ALCAs. ALCAs still serve as a valuable base of comparison for EcoFuel since they can provide an estimation on environmental impacts of current fuel production systems. After evaluating the literature landscape and available data sources, ALCAs were found to be a sufficiently reliant and accessible source of data for a baseline of comparison for EcoFuel.

Regarding the scope of the analyzed studies there are differences in system boundaries, functional units, approaches to multifunctionality and characterization of LCIs. Those differences all influence comparability.

Results for synthetic- and bio-based fuels WTT GWPs are comparable, worst and best cases can be identified and attributed to certain process specific hotspots.

A full environmental assessment of fuel production across a more holistic selection of midpoint indicators is much more difficult to carry out and infeasible with the available data. This is mostly because the examined studies focus on GWP, as defined in the inclusion criteria.

Due to uncertainties when aggregating many different production scenarios to mean values, the comparison baseline for EcoFuel is a range of GWP values rather than a single benchmark.

Data on non GWP midpoint indicators are scarcer and more uncertain. Therefore, it is only possible to identify tendencies in possible environmental hotspots based on a few studies. The hotspots in bio-based fuel and SynBio fuel production are fertilizer use and water usage in feedstock cultivation. Fertilizer related ammonia, phosphate and nitrate emissions have a high impact on acidification and eutrophication. The acidification potential for SynBio fuels is three times higher than for fossil fuels, the eutrophication potential is four times the value of the fossil reference. The high eutrophication and acidification potential of SynNoBio fuel production emerges mostly from upstream impacts of energy provision. The cumulated energy demand for most synthetic fuel pathways is approximately 2.5 MJ/MJ, translating to only 40 % of the spent energy stored in the fuel. Particulate matter emissions of synthetic fuel pathways are also higher than of the fossil reference, especially when using current grid mix energy based on fossil energy carriers. The system components with the highest influence on GWP results were identified to be LUC, crediting and the underlying energy mix. LUC is the main driver for bio-based fuels and SynBio fuels and contributes up to 86.8 % to the WTT carbon footprint.

For synthetic fuels the biggest impacts emerge from energy use, in some cases up to 98 % of the GWP are attributable to emissions from energy use.

Crediting has a big influence on non-fossil synthetic fuels and bio-based fuels WTT carbon footprint. The lifecycle stage at which credits are applied varies. This choice changes WTT results drastically, while WTW results remain unaffected. The magnitude of credits often surpasses the emissions from fuel combustion. The application of credits in the WTT phase can even lead to negative GWP results.

Process pathways for synthetic fuels are evaluated in more detail, enabling a more robust comparison.

As reported, the construction, operation (excluding all electric and thermal energy for H<sub>2</sub>, CO<sub>2</sub>, and fuel production), and decommissioning of CO<sub>2</sub> capturing facility, electrolyzer, and fuel production plant has a minor share in GWP (1-5 gCO<sub>2</sub>/MJ) in comparison to the whole fuel production process.

The GWP of the electrolyzing unit is mainly influenced by its lifetime. The mature AEL technology with a typical plant lifetime of > 30 years is usually integrated in large scale electrolysis plants producing > 10,000 Nm<sup>3</sup> of hydrogen per hour, contributing with 0.4-0.5 gCO<sub>2</sub>eq/MJ to the synthetic fuel GWP. Although high temperature SOEL is the most efficient technology for water splitting, it is in the early stage of commercialization and lifetimes of SOEL stacks are in the region of 10,000 hours. The output of SOEL electrolyzer units is no higher than 60 Nm<sup>3</sup> hydrogen per hour, resulting in a contribution of 3 gCO<sub>2</sub>eq/MJ to the GWP of the fuel. PEMEL electrolyzer are responsible for 1.2-1.3 gCO<sub>2</sub>eq/MJ of a fuel GWP.

In terms of CO<sub>2</sub> provision, the impact of point source capturing is negligible due to the high concentration of CO<sub>2</sub> in flue gas. This is not the case for DAC, where the effort to produce the same amount of CO<sub>2</sub> is much higher because of the low concentration in the atmosphere.

The main contributor in terms of GWP for synthetic FPPW is the energy provision for water splitting where the GWP is the highest when using energy from the grid mix. Carbon intensive electricity mixes with a high share of fossil fuels produce synthetic fuels with unfavorable GWP values. The 2015 German energy mix with a high share of coal powered energy and a carbon intensity of 527 gCO<sub>2</sub>eq/kWh produces synthetic fuels with GWPs of over 350 gCO<sub>2</sub>eq/MJ. However, low carbon intensive electricity such as the predominantly hydro powered grid mix in British Columbia (13 gCO<sub>2</sub>eq/kWh) provides the opportunity of producing synthetic fuels with WTT carbon footprints as low as 10 gCO<sub>2</sub>eq/MJ.

The information about the TRL of FPPWs is only available in around 5 % of all accumulated data points, therefore any comparison based on the TRL of a certain FPPW is extremely vague. It can be expected that with increasing TRLs, carbon footprints will decline considering the economies of scale, and technological advancement. Facility related environmental impacts are smaller on higher industrial scales. Higher process efficiencies would lead to lower environmental impacts.

Due to the modular character of the analysis, the findings from this study can be used to model synthetic fuel pathways and can be compared to single process data later in the EcoFuel development.

## 9 APPENDIX

During the process of literature review an extensive amount of data was collected and processed. The data table with all 355 datapoints for WTT GWP values is provided as an external spreadsheet. The GWP values, information on respective fuel specifications and source related information's are included in the supplementary material.

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## RENEWABLE ELECTRICITY-BASED, CYCLIC AND ECONOMIC PRODUCTION OF FUEL

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## ABSTRACT

The technoeconomic analysis section of this report is a comparative discussion of process routes from CO<sub>2</sub> to hydrocarbon fuels such as gasoline, kerosene and diesel (i.e. “drop in” fuels). Several technoeconomic assessments are reviewed comparing promising processes covering a wide range of TRLs, with a focus on routes involving electrolysis. A separate discussion of the technoeconomic merits of different CO<sub>2</sub> capture methods is included, as is a discussion of which CO<sub>2</sub> reduction products are themselves most economically feasible to target.

## INTRODUCTION TO TECHNO-ECONOMIC ANALYSIS

Conducting a techno-economic assessment (TEA) of early-stage and emerging technologies is becoming an increasingly popular approach to establishing process feasibility, notably in the fields of renewable fuels and chemicals and CO<sub>2</sub> utilisation. It often compliments a Life Cycle Assessment (LCA), which will evaluate, amongst several other environmental metrics, the greenhouse gas (GHG) emission reduction, usually taking into account the whole value chain: a ‘cradle-to-grave’ analysis<sup>1</sup>.

A TEA is an integrated evaluation (methodology framework) of the technological and economic feasibility of a process. It typically includes a process model, capital cost (CapEx) model, operating cost (OpEx) model and for deriving profitability indicators can be followed-up with a discounted cash flow (DCF) analysis<sup>2</sup>. The benefits of performing such an assessment of a technology that is still at the early-stage are that it identifies impactful operating parameters and cost bottlenecks for attaining economic feasibility and can help steer decisions for further R&D and associated resource and capital investments that can be significant. When several different new process and technology options are being considered, it can also act as a screening tool in prioritising research<sup>3</sup>.

Figure 1 depicts an overview of suggested main steps that are involved in a TEA.



Figure 1: Overview of the main steps involved in a techno-economic analysis



After defining the scope and what's to be included in the assessment (the system boundary) a starting-point can be a relatively simple conceptual block diagram of the process plant comprising of the primary unit operations and the main material input and output streams (raw materials/feedstocks and products). This can later be developed into a more sophisticated process flow diagram (PFD) that includes heat exchangers, pumps and compressors, as well as consideration of material recycle and the utility streams such as electricity, process steam and cooling water. The process model fulfils the mass and energy balance requirements, calculating raw materials (*e.g.* CO<sub>2</sub>, water) and utilities consumption rates. In the first instance the model can be implemented through the use of spreadsheet software, however, depending on the level of rigour required for the TEA, a commercial flowsheet simulator such as Aspen Plus® can be used. Such simulators incorporate an in-built physico-chemical property and thermodynamic model databank for the process streams and a suite of process unit operations, and readily compute the balances from user input data. They can also be used to perform preliminary equipment sizing, required for the CapEx model. For the simulation of more specialised equipment such as electrolysers, these may need to be approximated by the use of semi-analogous units, for example by assuming one or more of the available “general reactor” types, or be custom-modelled<sup>4,5</sup>.

The CapEx model used often depends on the Technology Readiness Level (TRL) and thus ultimately on available data and level of equipment design and specification making up the chemical process or plant. TRL descriptions to estimate the maturity of new technologies were originally conceived by NASA in the 1970s and more recently formulated by the EU for use in their H2020 programme and beyond. They are often employed for gauging the progress of R&D projects within academia, industry, and governments. The interpretation of TRLs pertaining to the chemical industry, as well as the implication to appropriate selection of TEA costing methods, is discussed elsewhere<sup>6</sup>. Note the EcoFuel project comprises of different unit operations at different starting TRLs, but in general the progress aspired to by the end of the project is from a proof-of-concept stage in the laboratory at TRL 3 towards a validation under industrially-relevant conditions at TRL 4-5. Cost estimates have associated with them an accuracy ranging from +/- 50% for an order of magnitude calculation to +/- 5 % for a detailed estimate that will utilise direct vendor data and costs, having attained a final stage process engineering and design level. Methods of CapEx estimation for early-stage technologies usually start from the basic ratio and proportion approach (capacity factored estimation) *e.g.*, the rule-of-six-tenths, or applying a more comprehensive parametric and factorial estimation method, as described in classic process economics texts<sup>7,8</sup>. Also, some cost methods can be accessed that are built-in to the commercial flowsheet simulators. Usually, a cost index is also used to account for price inflation of reference plant equipment, for a selected cost year basis of the study *e.g.*, Chemical Engineering Plant Cost Index (CEPCI), published in the Chemical Engineering magazine.

The OpEx model comprises of estimations of fixed and variable costs in order to derive manufacturing or production cost estimates. Several of these cost contributions are established from the process model's mass and energy balances, such as the raw materials and utilities consumption rates, which can be multiplied by a specific price obtained from the literature or in-house knowledge to derive a cost per unit of production *e.g.*, EUR/tonne of product. A contribution of the capital cost that forms part of the OpEx is annual depreciation, with often a simple straight-line depreciation approach being assumed over a typical scheduled period *e.g.*, 10 years. General operating cost models are described in textbooks and literature papers<sup>7,9</sup>. It should be noted that manufacturing or production cost estimates that are found in the literature, often involve different assumptions and not all cost contributions have been included in the calculation such as labour and taxes and in some cases capital depreciation. Some of the cost omissions are more significant than others at the early-stage, but the differences should be acknowledged when

comparing the values obtained from different sources. A sensitivity analysis of key parameters displayed in the form of a tornado plot or spider diagram helps to identify the most impactful variables, some of which can be influenced by research. The analysis is often univariate, adjusting one parameter at a time. Scenario analysis involves adjusting multiple parameters to construct worst-case (low performance) and best-case (high performance) options to compare with the base case.

Finally, a discounted cash flow analysis takes into account the time value of money in a series of future cash flows for a project's investment and derives profitability indicators such as net present value (NPV) and internal rate of return (IRR). The methodology can be implemented in a spreadsheet and can be considered as an optional add-on within the economic assessment of low TRL technologies. Anderson *et al*<sup>10</sup> describes the usefulness of such a model for investment decisions. Several publications on CO<sub>2</sub> utilisation also incorporate the cash flow method in their TEA<sup>40,11,12</sup>. Others use an alternative form of discounted cash flow analysis to calculate the levelised production cost, similar to a break-even or minimum selling price (equivalent to the price that would be charged for the product to generate a NPV of zero for the investment)<sup>13</sup>. This often employs a capital recovery factor (CRF), assuming a project lifetime and discount rate. Again, a sensitivity analysis can be conducted on the pertinent variables. Additionally, to help to understand the uncertainty associated with some of the main assumptions a Monte Carlo simulation can be run via a spreadsheet to create a probability distribution of values for a key parameter such as NPV<sup>14</sup>.

When setting-up a process model, many assumptions or specifications are involved relating to the performance of individual unit operations. For example, in order to perform the mass balance across reactor units in the absence of kinetics data, then these often comprise of conversion and selectivity values for a given stoichiometric chemical reaction(s). For separation vessels, those parameters that describe the overall performance are used such as a target purity level or a typical recovery percentage for a chemical product, based on the technology used. To start with, the assumptions can be made through estimation from consultation of the available literature and then updated later with empirical data derived in the project. As an example, one key unit operation within the EcoFuel process is the electrolyser and several figures of merit are used to describe the performance, as described below<sup>15,40</sup>.

**Current density:** The current density for a reaction determines the electrode area required to meet a production rate and the electrode area is a major factor in determining the cost and size of the electrolyser unit. It is evaluated as the current flow divided by the active electrode area (often assumed on a geometric basis) at a fixed operating potential. A high current density is usually desirable, reducing the electrode area, although there may be trade-offs with the energy costs for the required operating voltage and also the associated heat management. It relates to the electrochemical reaction rate per area of electrode (reflects the electrocatalyst activity) and is influenced by the electrocatalyst loading, its activity and the reactant mass transfer rates for the electrode (linked to the reactor design). For many industrial electrolytic processes, the current density should be >100 mA/cm<sup>2</sup> with one suggested value relevant for CO<sub>2</sub> reduction products being >300 mA/cm<sup>2</sup>, based on a preliminary economic analysis<sup>15</sup>. Achieving higher values of current density is certainly a development target for the R&D community.

**Faradaic efficiency (FE):** This represents the selectivity of the total electric charge supplied to the cell that is used to produce the desired product. For example, in a CO<sub>2</sub> electrolyser, if 100 electrons are supplied to the cathode and 40 of them are used to produce ethylene while the remaining 60 electrons are used in reactions to produce other reduction products such as hydrogen and carbon monoxide, the Faradaic efficiency for ethylene is 40 %. A high FE is beneficial to reduce the electricity demand for a given production rate of a target product with a reduced total current, as well as minimising energy wastage. It

also impacts on the necessary downstream separation process that would increase the capital and operating expenditure. An FE >50 % has been suggested in the literature for workable economics of such a process, although this will depend on the ease of separation for the target product and any by-products formed<sup>16</sup>.

The formula for Faradaic efficiency,  $\epsilon_F$ , is:

$$\epsilon_F = \frac{nZF}{It}$$

Where  $n$  is the number of moles of a given product produced over time  $t$ ,  $Z$  is the number of electrons required to produce 1 mole of the product,  $F$  is the Faraday constant, which is the charge of one mole of electrons, and  $I$  is the average current over time  $t$ <sup>17</sup>.

**Cell Voltage:** The potential difference between the anode and cathode of the cell, known as the cell voltage, impacts mainly operating costs by influencing the quantity of electrical power consumed by the cell.

$$E_{cell} = E_{anode} - E_{cathode}$$

$$P = I \times E_{cell}$$

Furthermore, high cell voltages can increase ancillary costs such as cooling electrolytes due to Ohmic heating.

Thermodynamics imposes a minimum cell voltage for a reaction, but steps can be taken to reduce the cell voltage as far as possible. One way is the use of highly active electrocatalysts which allow the desired electrode reactions to proceed at a given rate at a low *overpotential*.

**Overpotential:**  $\eta$ , is the difference between the electrode potential at which a reaction is actually driven and the thermodynamic equilibrium potential. For example, the overpotential of a cathode is:

$$\eta_{cathode} = E_{cathode} - E_{cathode}^0$$

Where  $E_{cathode}^0$  is the thermodynamic minimum potential and  $E_{cathode}$  is the measured electrode potential. The cell potential can also be reduced by decreasing the distance charges must travel between the anode and cathode, and by increasing the conductivity of electrolytes and membranes.

The thermodynamic cell potential is:

$$E_{cell}^0 = E_{anode}^0 - E_{cathode}^0$$

**Voltage Efficiency** can therefore be defined as:

$$\epsilon_V = \frac{E_{cell}^0}{E_{cell}}$$



**Energetic Efficiency:** This is also sometimes called “cell efficiency” and can be calculated by multiplying the Faradaic efficiency and the voltage efficiency:

$$\epsilon_{cell} = \epsilon_F \times \epsilon_V$$

This metric describes the ratio between the energy stored in the target product(s) versus the input energy needed to make it. A process that exhibits a high energetic efficiency indicates a small energy loss involved in producing the product and would be a good use for renewable electricity.

**Specific Energy Consumption:** So electricity costs can be estimated, the specific energy consumption, i.e., the number of kilojoules or kilowatt hours it takes to produce one kilogram of product, can be calculated:

$$SEC = \frac{I \times E_{cell}}{PR}$$

Where  $PR$  is the production rate of the desired product in units of mass per second.

**Cell stability:** This encompasses the extent of in-service degradation/deactivation of the electrode catalyst and indeed the electrochemical cell as a whole. The electrolyser needs to perform consistently at the required figures of merit for many thousands of hours. Proton exchange membrane (PEM) water electrolyzers have been shown to operate beyond 20,000 h (2.3 years)<sup>40</sup>, so a target lifetime for low temperature CO<sub>2</sub> electrolyser stacks might be similar. Overall, a better stability will reduce any required maintenance and stack replacement costs (and associated plant downtime costs with the loss of production), the latter being increasingly important if expensive electrocatalysts and components are used.

This introductory section has provided an overview of the structure and main components that comprise a techno-economic analysis. It should be acknowledged that although text-book methods are available, there is little standardisation and variations in approaches to TEA do exist, such as those developed and used in-house by industrial companies, often based on their own knowledge database. As previously mentioned, when comparing pertinent TEA output data between different sources, especially those works described in the literature, then it's useful to understand the possible reasons for any significant variations, such as selection of the system boundary, what cost components have been included and the assumptions made. With so many unknowns at the early-stage of technology development it can be expected for such discrepancies to occur between evaluations and the outputs from a TEA can generally be viewed as indicative only. The next sections look at some of the different technologies and process routes for the conversion of CO<sub>2</sub> to fuels, including examples of associated costs from literature-based TEA studies.

## CO<sub>2</sub> CAPTURE

The source of CO<sub>2</sub> is likely to have a large effect on both the economic and environmental performance of process chains for sustainable chemicals, materials and fuels. Most broadly, CO<sub>2</sub> can be captured from a concentrated point source, such as coal power station flue gas, by post-combustion capture (PCC) or alternatively it can be pulled straight from ambient air by direct air capture (DAC). A further alternative is pre-combustion capture, which is when a hydrocarbon fuel is gasified to syngas, the syngas then undergoes the water gas shift (WGS) reaction to convert CO to CO<sub>2</sub> and increase the concentration of hydrogen and the CO<sub>2</sub> is captured before the hydrogen is burned. Using DAC CO<sub>2</sub> allows CO<sub>2</sub> derived

products to be truly carbon-neutral, however using pre or post-combustion captured CO<sub>2</sub> means emissions are merely delayed. The economic benefits associated with carbon trading, taxes and offsetting therefore favour DAC over point sources. Furthermore, there is the benefit of not being constrained to locating the plant at a stationary emission point source of CO<sub>2</sub> and this makes DAC more suitable for distributed or localised utilisation scenarios.

However, an obvious benefit of point sources is their higher concentrations of CO<sub>2</sub>. The current atmospheric CO<sub>2</sub> concentration is around 414 ppm<sup>18</sup>, whereas typical flue gases from natural gas power stations are around 4 % CO<sub>2</sub><sup>19</sup> and pre-combustion mixtures of H<sub>2</sub> and CO<sub>2</sub> range between 15 to 50 % CO<sub>2</sub><sup>20</sup>. This significantly reduces the energy required to separate the CO<sub>2</sub> from air and therefore the energy costs of capture. The reason for this is that more work must be done working against the entropy of mixing.

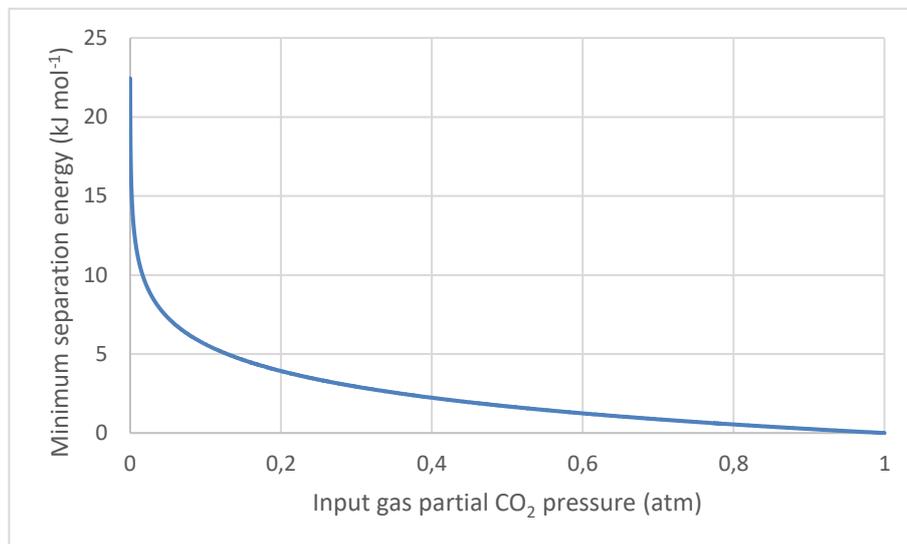


Figure 2: Thermodynamic minimum energy to separate CO<sub>2</sub> at 1 atm pressure and 298 K vs the partial pressure of CO<sub>2</sub> in the inlet gas stream

The free energy of separating CO<sub>2</sub> from a gas stream is given by :

$$\Delta G_{mix} = -RT \ln \frac{P}{P_0}$$

Where  $R$  is the gas constant and  $T$  is the ambient temperature,  $P$  is the partial pressure of CO<sub>2</sub> in the input gas stream and  $P_0$  is the desired pressure of pure CO<sub>2</sub><sup>21</sup>. Therefore, the thermodynamic minimum energy required to remove CO<sub>2</sub> from ambient air and produce a pure CO<sub>2</sub> stream at 1 atm pressure is 19 kJ mol<sup>-1</sup> whereas for a gas stream with a partial CO<sub>2</sub> pressure of 0.1 atm it is only 5.6 kJ mol<sup>-1</sup>. The energy dependence on CO<sub>2</sub> partial pressure can be seen in Figure 2. Using the current average EU electricity price of 0.219 EUR/kWh<sup>22</sup>, the cost of separating CO<sub>2</sub> from air at 100 % efficiency is 26 EUR per tonne and from a gas stream with a partial CO<sub>2</sub> pressure of 0.1 atm the cost is 7.7 EUR per tonne.

However, in a 2013 paper<sup>23</sup>, Klaus Lackner found that direct air capture is not fundamentally limited by thermodynamics and, in theory, can achieve higher energy efficiencies than capture from flue gases. This is because the purpose of flue gas scrubbing is to produce CO<sub>2</sub> free air and so the partial pressure of CO<sub>2</sub> on exit must be a small fraction of the partial pressure of the input stream. However, the purpose of DAC

is simply to absorb CO<sub>2</sub> and so a more efficient “skimming” approach can be taken in which the CO<sub>2</sub> partial pressure on exit is only slightly smaller than that on entrance and therefore the total energy of capture is closer to the reversible thermodynamic minimum. Thermodynamics can be an important tool for ruling out economically unfeasible processes on energy grounds, and it seems there are no fundamental reasons to rule out either DAC or PCC. In fact, it may be the case that the most efficient overall system for offsetting emissions is one in which the majority of CO<sub>2</sub> is captured at point source while the remainder is gradually “skimmed” from the atmosphere.

While the theoretical energy consumption of DAC does not rule it out, that does not automatically mean it is economically feasible. Even if energy consumption is equal per tonne of captured CO<sub>2</sub>, other costs including the cost of constructing and maintaining the plant, the footprint land area required for the DAC plant, the transportation of CO<sub>2</sub> to the location of utilisation, among others, must be considered. While there are currently no large scale DAC plants operational, Carbon Engineering plans to begin operating a plant capable of capturing 0.5 megaton of CO<sub>2</sub> per year in the United States in 2024<sup>24</sup>. Carbon Engineering's DAC process absorbs CO<sub>2</sub> by contacting air with a potassium hydroxide solution to form potassium carbonate, which is then thermochemically regenerated. A 2018 paper calculated the levelized cost of \$ 94 to \$ 232 per ton of CO<sub>2</sub><sup>25</sup> for this process. Climeworks, whose amine functionalised cellulose sorbents are currently used in the world's largest operational DAC plant<sup>26</sup>, estimates costs of around \$ 600 per ton of CO<sub>2</sub>, which it aims to reduce to between \$ 200 and \$ 300 by 2030<sup>27</sup>. However, Fasihi *et al*<sup>39</sup> found in their technoeconomic analysis of DAC that the high temperatures required for Carbon Engineering's process would make it less cost effective than lower temperature methods in the long run. Capture methods that use basic solutions for capture but regenerate the solutions electrochemically rather than thermochemically have been proposed as alternatives<sup>28</sup>. The International Energy Agency estimates the cost of DAC at \$ 134 to \$ 342 per ton<sup>29</sup> and overall, in the literature, there is still very wide variation in cost estimates for DAC of between \$ 100 and \$ 1000 per ton of CO<sub>2</sub><sup>30</sup>.

The International Energy Agency estimates the cost of capture from power generation at between 50 and 100 \$ per ton<sup>30</sup>, which currently puts the top of its cost range at the bottom of the range of DAC. This suggests a future in which both technologies are used under different circumstances. Taking the perspective of CO<sub>2</sub> emitters, a 2020 study comparing DAC and point source capture for decarbonising United States natural gas power found that it would make most economic sense to retrofit post-combustion capture to power plants where possible, but that DAC would be effective in offsetting emissions from non-retrofitable plants and addressing the residual emissions from retrofitable plants<sup>31</sup>. It was estimated that at a DAC cost of \$ 550 / ton, DAC would be competitive to capture one third of US natural gas CO<sub>2</sub> emissions and at a cost of \$ 100 / ton would be more competitive than retrofitting post-combustion capture for 45 % of emissions. By considering the likely efficiencies from scale up and “learning by doing” as each technology is rolled out, the study found DAC to have potential for more dramatic cost reduction in future. However, it is important to remember that DAC and post-combustion capture are at different stages of development meaning that the potential cost reductions for DAC at a technology readiness level of 6<sup>32</sup> are less certain than those projected for post-combustion capture which has a TRL of 9<sup>33</sup>. Interestingly, Schmidt *et al*<sup>98</sup> calculated a less than 10 % decrease in overall energy efficiency for two CO<sub>2</sub> to fuels processes when DAC rather than PCC was used as the CO<sub>2</sub> source.

Comparing DAC and PCC, the CO<sub>2</sub> produced by each process is not necessarily the same. A 2015 study<sup>34</sup> split impurities in post-combustion captured CO<sub>2</sub> into three categories: those arising from fuel burning, air ingress, and process fluid. Coal power station flue gasses may contain impurities such as: SO<sub>x</sub>, NO<sub>x</sub>, HCl, HF, CO, H<sub>2</sub>S, COS, NH<sub>3</sub>, and HCN from combustion as well as trace metals such as Hg, Pb, Se and As

and particulates such as ash and soot<sup>34</sup>. J-Y Lee et. al<sup>35</sup> estimated the impurities present in post-combustion capture CO<sub>2</sub> streams for scenarios involving different combinations of air pollution control devices. A summary of the results is given in Table 1.

Table 1: Estimated gas concentrations in post-combustion capture CO<sub>2</sub> based on the minimum and maximum deployment of air pollution control devices<sup>35</sup>

Gas	Worst case	Best case
CO <sub>2</sub>	95.5 – 99.4 wt %	99.7 - > 99.9 % wt %
SO <sub>2</sub>	0.6 – 4.4 wt %	34 – 135 ppmv
SO <sub>3</sub>	42 – 579 ppmw	21 – 302 ppmw
NO <sub>2</sub>	24 – 111 ppmw	7 – 35 ppmw
HCl	36 – 835 ppmw	2 – 27 ppbw
Hg	23 – 261 ppbw	2 – 27 ppbw

Of course, the more air pollution control devices added, the greater the capital costs of installation and the greater the energy costs of running them. Of particular concern for down-stream thermo and electro-catalytic reduction processes are sulfur compounds, and while legislation mandates SO<sub>x</sub> removal to some degree in many countries, this may not be sufficient to avoid catalyst poisoning. Y. Zhai *et al*<sup>36</sup> found that exposure of a copper electrocatalyst for CO<sub>2</sub> reduction to around 1500 ppm of NO<sub>2</sub> was beneficial or neutral, exposure to around 100 ppm of SO<sub>2</sub> was mildly detrimental or neutral. Dissolved sulfide was extremely detrimental, but dissolved sulfate was beneficial. Gold electrocatalysts for the reduction of CO<sub>2</sub> to CO have been found to become poisoned by sulfur compounds<sup>37</sup>.

DAC is obviously less susceptible to the impurities from fuel burning since the concentrations of such impurities are much lower in air than in flue gas, however impurities from air ingress and the capture media are likely to persist.

It is important to remember when comparing DAC and PCC in economic terms, that economic arguments may be of less significance in the future. The Intergovernmental Panel on Climate Change has concluded that rapid emissions cuts will not be sufficient to keep the global temperature rise below 1.5 °C and that negative emissions technologies such as DAC will be essential<sup>38</sup>. Furthermore, in a net-zero world, DAC will be essential for offsetting the residual emissions from PCC, which only captures between 50 – 94 % of CO<sub>2</sub> on average<sup>39</sup>.

## CO<sub>2</sub> REDUCTION PRODUCTS

A wide range of products have been observed during the electrochemical reduction of CO<sub>2</sub>. However, not all products are made with the same efficiency or at the same rate. It is important to consider the energetic and catalytic requirements of each product, as well as their demand and market price, to fully evaluate their economic viability.

The most commonly reported electrochemical CO<sub>2</sub> reduction products include carbon monoxide, formic acid (from formate), methanol, methane, ethylene, ethanol, and propanol. Hydrogen is also produced as a product of water reduction. In most cases, this would be seen as an undesirable by-product, however it can be deliberately produced along with carbon monoxide and sold as syngas. Comparing the half-cell reactions and the corresponding reduction potentials in Table 2 immediately highlights potential problems with producing C<sub>2+</sub> molecules: thermodynamically speaking, the products listed should all be

produced simultaneously, since they have very similar reduction potentials. This raises the question: Can any of these products be produced selectively, and what catalysts exist to achieve this? Furthermore, which of these products are profitable and is there enough demand for them to justify investment?

Table 2: The electrochemical half equations of CO<sub>2</sub> to commonly reported products, with their associated reduction potentials versus standard hydrogen electrode.<sup>40</sup>

Half-cell reaction	Potential vs SHE
$\text{CO}_{2(g)} + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{CO}_{(g)} + \text{H}_2\text{O}_{(l)}$	-0.106
$\text{CO}_{2(g)} + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{HCOOH}_{(aq)}$	-0.250
$\text{CO}_{2(g)} + 6\text{H}^+ + 6\text{e}^- \leftrightarrow \text{CH}_3\text{OH}_{(aq)} + \text{H}_2\text{O}_{(l)}$	0.016
$\text{CO}_{2(g)} + 8\text{H}^+ + 8\text{e}^- \leftrightarrow \text{CH}_4_{(g)} + 2\text{H}_2\text{O}_{(l)}$	0.169
$2\text{CO}_{2(g)} + 12\text{H}^+ + 12\text{e}^- \leftrightarrow \text{C}_2\text{H}_4_{(g)} + 4\text{H}_2\text{O}_{(l)}$	0.064
$2\text{CO}_{2(g)} + 12\text{H}^+ + 12\text{e}^- \leftrightarrow \text{C}_2\text{H}_5\text{OH}_{(aq)} + 3\text{H}_2\text{O}_{(l)}$	0.084
$3\text{CO}_{2(g)} + 18\text{H}^+ + 18\text{e}^- \leftrightarrow \text{C}_3\text{H}_7\text{OH}_{(aq)} + 5\text{H}_2\text{O}_{(l)}$	0.095
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_{2(g)}$	0.000



Table 3: Faradaic Efficiencies of CO<sub>2</sub> Reduction Products on Metal Electrodes in CO<sub>2</sub>-Saturated 0.1 M KHCO<sub>3</sub> (pH = 6.8)<sup>41</sup>

Metal	$E$ [V vs RHE]	$J_{\text{total}}$ [mA/cm <sup>2</sup> geo]	CH <sub>4</sub> [%]	C <sub>2</sub> H <sub>4</sub> [%]	EtOH [%]	PrOH [%]	CO [%]	HCOO <sup>-</sup> [%]	H <sub>2</sub> [%]	Total [%]
Pb	-1.24	-5.0	0	0	0	0	0	97.4	5	102.4
Hg	-1.12	-0.5	0	0	0	0	0	99.5	0	99.5
Tl	-1.21	-5.0	0	0	0	0	0	95.1	6.2	101.3
In	-1.16	-5.0	0	0	0	0	2.1	94.9	3.3	100.3
Sn	-1.09	-5.0	0	0	0	0	7.1	88.4	4.6	100.1
Cd	-1.24	-5.0	1.3	0	0	0	13.9	78.4	9.4	103
Au	-0.65	-5.0	0	0	0	0	87.1	0.7	10.2	98
Ag	-0.98	-5.0	0	0	0	0	81.5	0.6	12.4	94.6
Zn	-1.15	-5.0	0	0	0	0	79.4	6.1	9.9	95.4
Pd	-0.81	-5.0	2.9	0	0	0	28.3	2.8	26.2	60.2
Ga	-0.85	-5.0	0	0	0	0	23.2	0	79	102
Cu	-1.05	-5.0	33.3	25.5	5.7	3	1.3	9.4	20.5	103.5
Ni	-1.09	-5.0	1.8	0.1	0	0	0	1.4	88.9	92.4
Fe	-0.52	-5.0	0	0	0	0	0	0	94.8	94.8
Pt	-0.68	-5.0	0	0	0	0	0	0.1	95.7	95.8
Ti	-1.21	-5.0	0	0	0	0	tr.	0	99.7	99.7

Firstly, can any of these products be produced selectively? In 1985, Hori *et al* initially explored CO<sub>2</sub> reduction on a number of polycrystalline metal electrodes, the results of which are shown in Table 3.<sup>41</sup> It was found that carbon monoxide and formic acid can be produced relatively easily at high Faradaic efficiencies using simple metallic electrodes. Since then, the low temperature reduction of CO<sub>2</sub> to CO has reached TRL4/5 with the use of silver nanoparticle catalysts. This process has reached selectivities as high as 98% and approaches 50% cell efficiency.<sup>42,43</sup> Alternatively, solid oxide electrolyser cells (SOEC), which run at high temperature, are approaching TRL7/8 and do CO<sub>2</sub> to CO reduction with significantly higher current density, 100% Faradaic efficiency and 80% cell efficiency.<sup>44</sup> This makes CO an attractive product molecule, at least in the short term, since the technology to produce it is more mature.

Hori *et al* also showed that copper metal uniquely reduces CO<sub>2</sub> to a range of C<sub>2+</sub> products. This opened the possibility of producing higher value products in a single electrolysis step, rather than multiple. The problem is, if multiple products are produced simultaneously, separation downstream becomes a more significant, and therefore expensive, task. Thermodynamically speaking, with such similar reduction potentials, it is difficult to selectively produce any one product over the others. This is seen even for state of the art copper catalysts, such as oxide-derived copper nanoparticles, where a mixture of products are detected.<sup>45,46</sup> The ability to selectively produce one C<sub>2+</sub> product is a goal of current research, and more understanding of catalyst design, reaction mechanisms, kinetics, and cell design is needed to make this possible. In recent literature, it has been shown possible to unselectively produce C<sub>2+</sub> products with a combined Faradaic efficiency of up to 90%, which is an incredible achievement in itself.<sup>47</sup> Whether that mixture of products is viable for up-scaling would depend on the cost of separation.

The number of electrons a product needs has a direct impact on the energy costs. Jouny *et al*<sup>40</sup> compiled data for Table 4, which shows the number of electrons required to make each product, the market price and the subsequent price per electron used. Since electrical energy is used to drive the production of these molecules, the cost of electricity will have a large impact on profitability. Similarly, the cost of CO<sub>2</sub> is also a significant cost for these systems, so products that require more CO<sub>2</sub> will be more expensive.

Surprisingly, even though formic acid offers by far the highest price per electron listed, the low global production of this product reflects its limited industrial use. As a result, formic acid electrolyzers don't offer much scale up opportunity. If the goal is to make a significant impact on the chemical industry, more innovative uses for formic acid as a feedstock would need to be developed. In contrast, methane has the highest global production, owing to its important domestic and industrial uses as a fuel and chemical feedstock, as well as its relative natural abundance. However, it has the lowest normalised price per electron, meaning methane has the opportunity for large scale up, but lacks the profitability of formic acid. N-propanol is listed as having the lowest annual production despite its versatile and important uses industrially, which is mainly due to difficulties in production. N-propanol is thought to have significant market potential as a fuel source and energy storage chemical, making it a highly desirable product of CO<sub>2</sub> reduction. Existing systems struggle to achieve a significant Faradaic efficiency however, so it currently remains unfeasible. Jouny *et al*<sup>40</sup> conclude that the highly desirable products are ethylene, methanol, and ethanol, since these products have high market capacity as well as decent normalized market prices.

Table 4: The number of electrons, market price, normalized price and annual global production of the common CO<sub>2</sub> reduction products.<sup>40</sup>

Product	Number of electrons required	Market price (\$/kg)	Normalised price (\$/electron) x 10 <sup>3</sup>	Annual global production (Mtonne)
Syngas (CO + H <sub>2</sub> )	2	0.06	0.8	150.0
Carbon monoxide	2	0.6	8.0	
Formic acid	2	0.74	16.1	0.6
Methanol	6	0.58	3.1	110.0
Methane	8	0.18	0.4	250.0
Ethylene	12	1.30	3.0	140.0
Ethanol	12	1.00	3.8	77.0
n-Propanol	18	1.43	4.8	0.2

As renewable energy capacity increases, the price of renewable electricity is expected to decrease. Similarly, the cost of CO<sub>2</sub> (from most sources) is expected to decrease as capture technologies mature. Since some products require more electricity and CO<sub>2</sub> to produce than others, the economic viability of the products will rely heavily on the costs of these inputs. Based on these market parameters, as well as more technology-specific parameters like operating voltage, product selectivity and cell efficiency, a study by Huang *et al*<sup>48</sup> suggests three economic scenarios in their comparison of CO<sub>2</sub>RR products: (1) a “current” scenario with parameters from recent literature and recent market prices; (2) a “future” scenario based on more aggressive technical parameters and using comparisons to other, more advanced, technologies, such as fuel cells; and (3) a “theoretical” scenario with parameters approaching technical limitations, free CO<sub>2</sub> and \$0.02 kWh<sup>-1</sup> electricity. From this, they calculated a minimum selling price for each product, which is the price at which the product must sell to generate a net present value of zero for a 10% internal rate of return. These minimum selling prices are compared with the ten-year average market price for each product.

Of the electrocatalytic systems studied, none of the products were found to be cost competitive under the “current” scenario. In the “future” scenario, after applying the improved technical and cheaper market parameters, CO and formate were calculated to meet or beat the market prices. For ethylene and ethanol, the minimum selling price did not beat the ten-year average market price, but did fall within the price range (below the upper bound) over that time period. In the “theoretical” scenario, CO, formate, ethylene, ethanol and methanol all beat the current market price, while methane remains unprofitable. This study emphasises the importance of CO<sub>2</sub> and electricity prices on the profitability of products.

This study does not account for the argument that renewable, and carbon neutral (or negative) fuels can be marketed as such, and therefore charge a higher price on the market and still be in demand. In addition, this study uses prices from the U.S. market, however prices can vary significantly between global regions. For example, in December 2021, the price of natural gas was \$40 per MMBtu in Europe versus \$6.5 per MMBtu in the U.S.<sup>49</sup> It's possible that reduction to methane could be more profitable in these regions, especially considering CO<sub>2</sub> electrolysis can be coupled to any industrial CO<sub>2</sub> flue gas, like fossil fuel power plants and steel works.

A similar analysis by P. De Luna *et al*<sup>50</sup> emphasises the cost of electricity as a key factor to making these systems competitive with fossil fuels. The study claims that when electricity costs fall below \$0.04 kWh<sup>-1</sup>

and energy efficiency is above 60%, all the products analysed ( $H_2$ , CO, ethanol and ethylene) became profitable. In addition, it was predicted that electrolysis, when powered by renewable electricity, has the lowest carbon emissions of all competing renewable processes, such as bio-catalytic and thermo-catalytic refineries.

One possible utilisation of  $CO_2$  electrolysis is as an energy storage solution. With more renewable energy sources being used to power national grids, the turbulent nature of these technologies presents a supply and storage problem. With solar energy, for example, power can only be generated during daylight hours, and cloud coverage further decreases this output. In comparison, energy demands often increase in the evenings and at night when people need to turn on lights and cook. As such, energy produced during the day has to be stored and then released at times of high demand. Batteries offer one method of energy storage. However, the chemical fuels are up to 100 times more energy dense than lithium-ion batteries<sup>51</sup>, so storing electrical energy as chemical fuels offers a more attractive solution at large scale and over long periods of time. In addition, batteries are unsuitable for storing energy over long periods of time, as they have poor long term stability.

Energy density and storage capacity are important for both energy storage and transport and so producing longer chain hydrocarbons is desirable. A study by O. Bushuyev *et al*<sup>52</sup> suggests that even though energy density increases with chain length, normalising this against the number of electrons needed to produce each product shows that the smaller products, up to  $C_2$  are likely to be more profitable. Achieving a similar overall energy storage capacity would require longer chain molecules to be produced at higher Faradaic efficiencies. Unfortunately, current technology produces longer chain hydrocarbons at lower Faradaic efficiency, with no products above  $C_4$  being detected at all. The study notes that due to the high cost of product separation, producing higher-carbon products selectively is necessary to make it competitive. Technoeconomic modelling in this study also concludes that currently, CO and formic acid are the most economically viable, but more reduced products, such as propanol, have the most economic potential in the future. It is suggested that greater understanding of reactor and catalyst design, will drive this technology forwards.

In general, most technoeconomic models for  $CO_2$  electroreduction agree on a few key things:  $CO_2$ RR to CO and formic acid are currently the most advanced technologies in terms of TRL, and are closest to being economically competitive. These products can be produced at very high Faradaic efficiencies, so product separation costs are lower and cell efficiency is higher when compared to  $C_2$  products. Formic acid is not always as easy to separate and concentrate depending on whether formate or formic acid is formed during electrolysis.<sup>53</sup> CO can be fed into other processes, such as Fischer-Tropsch, to further add value. It is generally agreed that the reduction of  $CO_2$  to  $C_{2+}$  products has a lot of market potential. Products such as ethanol, ethylene and propanol have high market prices and are versatile as chemical feedstocks, giving them significant demand. However, current larger-scale electrolyzers have relatively low Faradaic efficiency and selectivity for these products, so cell efficiency is low and the cost of separation is high. In addition, these more reduced products require 6-9 times more electrons to produce, so the cost of electricity is more significant. It is hoped that cheaper  $CO_2$  from direct air capture, cheaper electricity from renewable sources and developments in electrolyser design will all come together to make this technology competitive.

## COMPARISON OF ROUTES FROM CO<sub>2</sub> TO FUELS

The scope of this section of the review is limited to comparing routes which begin with CO<sub>2</sub> as their feedstock and produce as their end products relatively long chain hydrocarbon liquid transport fuel such as gasoline, aviation fuel or diesel.

Now that the goal of producing sustainable fuels from CO<sub>2</sub> is established, it is important to compare the technical and economic performance of the numerous possible routes from CO<sub>2</sub> to fuel. The proposed EcoFuel process can be summarised as in Figure 3.

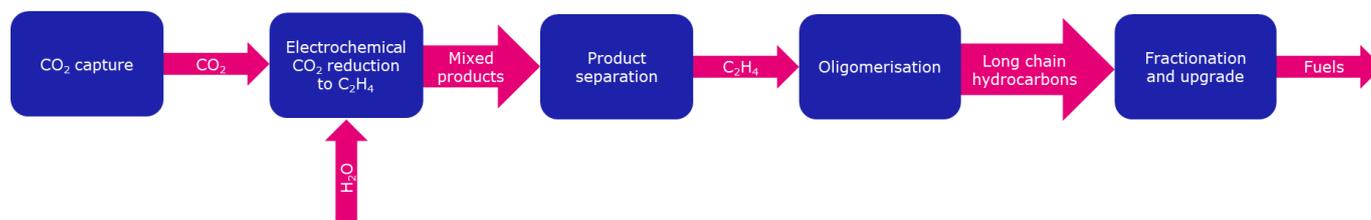


Figure 3: Concept block diagram of the EcoFuel process

In this process, air captured CO<sub>2</sub> is electrochemically reduced in one step to ethylene, which is separated from side product gases such as CO and H<sub>2</sub> and unreacted CO<sub>2</sub>, before being oligomerised to longer chain hydrocarbons. As data for the performance of this process is not yet available, it will merely be used as a discussion point for comparison with alternative routes which have already been published.

## CELL CONFIGURATIONS FOR LOW TEMPERATURE CO<sub>2</sub> ELECTROLYSERS

The routes to fuels considered in this review deploy electrolyzers of different types for specific purposes, or sometimes as competitors for achieving the same purpose. For example, one route may use a proton exchange membrane water electrolyser (PEMWE) to produce hydrogen while another may use a solid oxide electrolyser cell (SOEC) to produce carbon monoxide. However, similar routes could use either a two-gap, one-gap or zero-gap CO<sub>2</sub> electrolyser to produce ethylene. To understand the techno-economic arguments for choosing one route over another, it is therefore important to review the wide variety of electrolyzers upon which much of the rest of the route pivots.

Low temperature CO<sub>2</sub> electrolyzers can be split into categories based on the number of electrolyte “gaps” between the electrodes and the ion exchange membranes. These cells must have ion exchange membranes that allow solution charges to flow, but prevent the gases produced at the anode and cathode from mixing.

An example of two-gap cell employing a cation exchange membrane is depicted in Figure 4. The anode in a two-gap cell is typically a plate of titanium coated with iridium oxide as the electrocatalyst. An advantage of the two-gap cell is its simplicity and the good durability of the anode. In a one-gap cell, as depicted in Figure 5, the anode catalyst is in direct contact with the membrane, which can reduce the cell voltage by decreasing the distance charges must travel between the electrodes. The coated membrane is referred to as a half CCM (catalyst coated membrane). A porous transport layer (PTL), often a platinised titanium felt, provides electrical contact between the external circuit and the anode catalyst while allowing electrolyte and gas to flow.

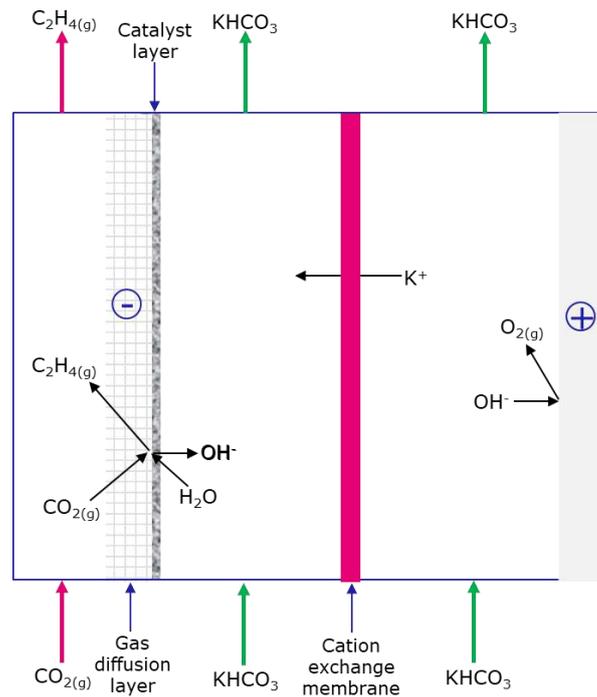


Figure 4: Schematic diagram of an example of a two-gap cell

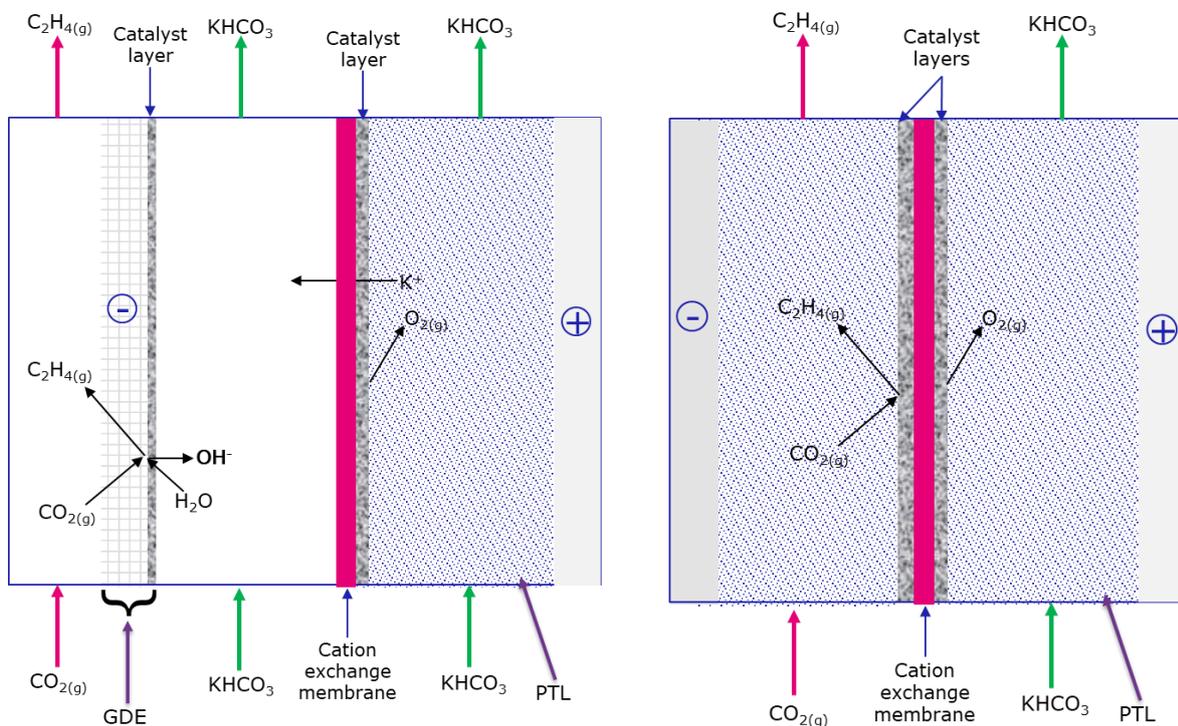
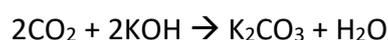


Figure 5: Schematic diagram of a one-gap cell (left) and a zero-gap cell (right)

For a given electrolyte, the cell voltage can be decreased further in a zero-gap cell, which is similar to a PEMWE in that the cathode and anode catalyst layers are directly coated onto the membrane to form a CCM and there are two porous transport layers. The cathode PTL is often a carbon paper and is popularly called a “gas diffusion layer” or GDL. Today it is not certain exactly which cell configuration will be used commercially. While studies conducted using the zero-gap cell will tend to give favourable cell voltages, difficulties have been observed in running this configuration over long periods, such as acidification of the

cathode, leading to unwanted HER<sup>54</sup> or high rates of CO<sub>2</sub> crossover. Furthermore, to avoid drying out of the cathode catalyst layer and membrane, humidified CO<sub>2</sub> is fed to the catholyte and therefore the energy cost of vaporising water to feed the catholyte must be considered<sup>54</sup>.

Low temperature one-gap electrolyzers that use very alkaline electrolytes such as concentrated KOH can achieve high Faradaic efficiencies for ethylene and lower cell voltages than neutral zero-gap cells due to the very conductive electrolyte, but this comes at the expense of high CO<sub>2</sub> losses as CO<sub>2</sub> reacts with hydroxide to form carbonate.



This means that the energy costs of regenerating the electrolyte and recovering CO<sub>2</sub> from the electrolyte must be considered. The extent of this problem with alkaline electrolyte was laid bare in a recent study which calculated the cost of regenerating CO<sub>2</sub> and electrolyte to be \$ 300 / ton of ethylene produced<sup>55</sup> directly from CO<sub>2</sub> in an alkaline one-gap cell.

In 2021, Sisler *et al*<sup>56</sup> conducted a techno-economic study to find the most cost-effective electrochemical route from CO<sub>2</sub> to ethylene. Ignoring CO<sub>2</sub> loss to carbonate formation, they conducted a sensitivity analysis on the factors affecting the cost of ethylene produced from CO<sub>2</sub> in an alkaline one-gap cell<sup>56</sup>. The most cost-sensitive parameters were electricity price, Faradaic efficiency and cell voltage, however current density did not significantly affect cost once above 1 A cm<sup>-2</sup>. Separately, the variation of the cost of ethylene with the rate of CO<sub>2</sub> loss was modelled for a neutral zero-gap cell and an alkaline one-gap cell. In alkaline one-gap cells CO<sub>2</sub> is lost as carbonate, which crosses the anion exchange membrane to the anode, whereas in neutral zero-gap cells it is lost mainly due to direct crossover of CO<sub>2</sub> gas. Alkaline one-gap cells were found to be more sensitive to CO<sub>2</sub> loss due to the high cost of electrolyte regeneration (in this example using a calcium caustic recovery loop) compared with CO<sub>2</sub> separation from anode oxygen with a CO<sub>2</sub> capture system. In fact, electrolyte regeneration was found to be the largest contributor to the ethylene cost for an alkaline one-gap cell. Overall, the calculated cost of ethylene produced in the neutral one-gap cell was just under \$ 6000 per ton of ethylene compared to just under \$ 8000 for the alkaline one-gap cell. Therefore, it is likely that the most suitable configuration for commercialisation is the zero-gap cell with a neutral electrolyte.

## CO<sub>2</sub> TO ETHYLENE IN ONE OR TWO STEPS?

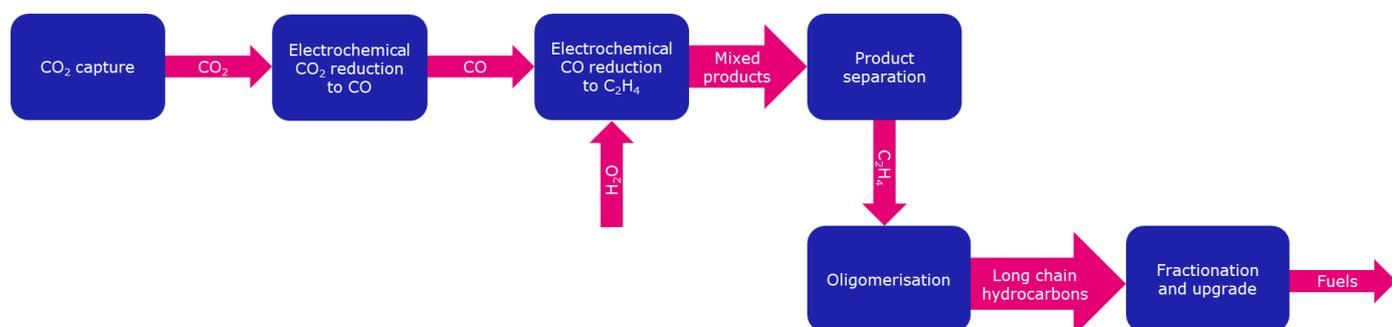


Figure 6: Concept block diagram of an alternative process in which ethylene is produced in two steps

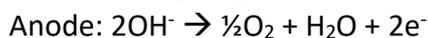
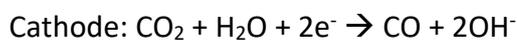
An important question is whether it will be more economical to produce ethylene directly from CO<sub>2</sub> or to first reduce CO<sub>2</sub> to CO and then reduce CO to ethylene. A starting point is the obvious fact that two different types of electrolyser are needed when the reduction to ethylene is split. This would increase

the complexity of the system and would be expected to increase the required balance of plant to run the electrolysis. Furthermore, unless the gas stream from the CO<sub>2</sub> to CO electrolyser is 100 % CO, which is very unlikely, an additional gas separation step may be required which could significantly contribute to energy costs, and furthermore increase the complexity of the plant.

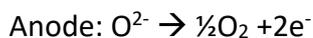
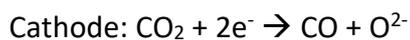
CO can be produced by either low temperature electrolysis or by high temperature electrolysis in a solid oxide electrolyser cell (SOEC). The two technologies are perhaps surprisingly different and so before considering the merits of reducing CO<sub>2</sub> in two steps it is important to consider which technology is most suitable. In either case the whole reaction is:



In the low temperature cell, the half reactions are as follows:



And in the SOEC they are:



In the latter case, the O<sup>2-</sup> ions formed at the cathode travel through the solid oxide electrolyte (i.e., yttria stabilized zirconia) to the anode, as illustrated in Figure 7. For sufficient conductivity of these ions, SOECs are typically operated between 700 and 900 °C<sup>57</sup>.

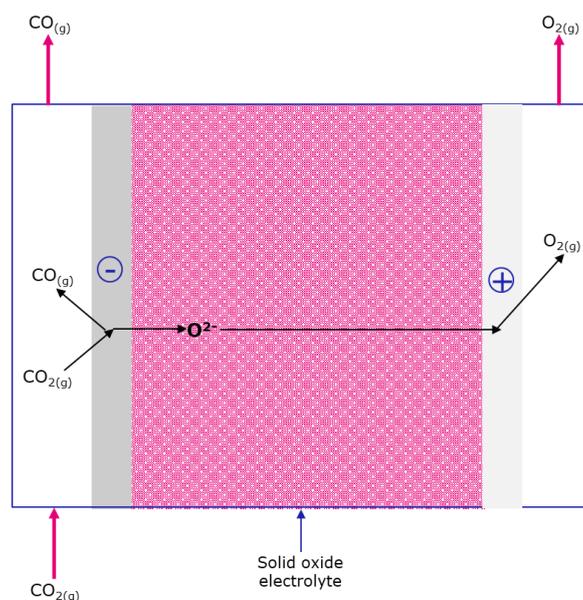


Figure 7: Schematic diagram of a solid oxide electrolyte cell electrolysing CO<sub>2</sub>

At first glance, it is difficult to see why there would be any benefit in electrolysing CO<sub>2</sub> at high temperature if it is possible to do it at low temperature, however a brief discussion of thermodynamics provides a convincing rationale. The splitting of CO<sub>2</sub> into CO and O<sub>2</sub> is endothermic and endergonic, which means that in electrolysis, both heat and electrical energy are required<sup>58</sup>. As the temperature increases, the

proportion of energy that can be supplied as heat increases too, this means that greater efficiency can be gained because more of the heat lost to resistive heating of the cell can be used in the reaction.

Today, SOECs can produce CO with close to 100 % Faradaic efficiency at current densities above 800 mA cm<sup>-2</sup>, whereas low temperature electrolyzers tend to operate at below 400 mA cm<sup>-2</sup> and typically give lower Faradaic efficiencies due to the parasitic hydrogen evolution reaction, which is an inherent disadvantage of using an aqueous electrolyte<sup>57</sup>. However, Faradaic efficiencies close to 100 % have been achieved, with the caveat that this was with the very high pH of alkaline electrolyte<sup>59</sup>. Cell voltages as low as 1.0 V are achieved by SOECs<sup>60</sup> compared to 2.5 V for low temperature electrolyzers<sup>61</sup>, giving them much higher electrical efficiencies of around 90 % compared to at best 50 % for low temperature electrolyzers.

The high operating temperatures of SOECs mean that the kinetics of electrode reactions are much faster and so precious metal catalysts are not required. Commonly used cathode catalysts for low temperature electrolyzers are Ag and Au, while the anode catalyst is commonly IrO<sub>2</sub>, which means material costs are likely to be higher unless alternative catalysts are developed.

Mainly as a result of their higher energy efficiencies, the minimum selling price for CO produced using SOEC is one order of magnitude lower than for that produced by low temperature electrolysis and is close to the current US market price<sup>40</sup>. Therefore, considering the current technological states of high and low temperature electrolysis to CO, it makes most sense to use a SOEC.

One of the main proposed advantages of splitting the reduction to ethylene into two steps is a reduction or even total elimination of CO<sub>2</sub> losses during electrolysis if the CO is produced in a SOEC, since no carbonate ions are formed, and the solid electrolytes are impermeable to gas. Furthermore, as long as pure CO<sub>2</sub> is fed to the cathode, an SOEC cathode product is completely free of H<sub>2</sub> and H<sub>2</sub>O, which is definitely not the case for low temperature cells.

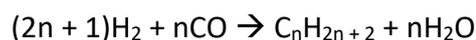
As shown in Figure 6, the CO from the SOEC is fed into a CO-to-ethylene electrolyser in which, of course, no CO<sub>2</sub> is lost as carbonate. Furthermore, since CO is polar, unlike non-polar CO<sub>2</sub>, gas crossover through the membrane should be significantly lower. A 2021 study calculated a tandem SOEC and an alkaline one-gap cell to have significantly lower cost per tonne of ethylene than operating a single neutral zero-gap cell based on current lab data as well as a lower future cost under “optimistic” scenarios for future technological development of both technologies<sup>56</sup>. This was due to the high electrical energy efficiencies already attained with SOEC CO<sub>2</sub> electrolyzers and alkaline CO electrolyzers when compared to zero-gap neutral CO<sub>2</sub> electrolyzers, which generally operate with higher cell voltages. It was assumed that excess heat from upstream and downstream processes could be used to keep the SOEC and its inputs at temperature, however since SOECs typically run at 750 °C, it is questionable where such high grade heat could be supplied from, since for example ethylene oligomerisation to jet fuel can be carried out at around 300 °C<sup>62</sup>. However, it is possible to run SOECs at or above the “thermoneutral voltage” at which resistive heating provides the necessary thermal energy for the reaction and therefore no external heat input is required. In this case, only the input gas must be heated. Some heating for this can come from exothermic downstream processes and if the cell is run above the thermoneutral voltage the feed gas can be pre-heated to close to the operating temperature of the cell by using a heat exchanger/interchanger for the feed and product streams.

So, overall, with the state of technology today, it appears that producing ethylene in two steps using a tandem SOEC and alkaline one-gap electrolyser system is the most economical. However, advances in

low temperature electrolyser design may significantly reduce CO<sub>2</sub> losses and increase energy efficiency in the future<sup>63</sup>. For example, a recent paper employed water as the electrolyte (only on the anode side) and a layer of anion exchange ionomer on the cathode as a “permeable CO<sub>2</sub> regeneration layer” or PCRL, which provided a high local pH at the copper catalyst surface which promoted a high C<sub>2+</sub> Faradaic efficiency, while the low pH at the boundary between the PCRL and the cation exchange membrane promoted the release of CO<sub>2</sub> from the electrolyte, which allowed it to be consumed in the reduction. This helped the experimenters to achieve a single pass CO<sub>2</sub> conversion of 85 %<sup>64</sup>. Single step electrolysis of CO<sub>2</sub> to ethylene is a new technology at a low level of maturity for which it may be possible to significantly improve the efficiency and so, in the long term, the question of the most economical way to electrochemically produce ethylene from CO is not settled.

## FISCHER-TROPSCH

Rather than using ethylene as a building block for hydrocarbons, CO itself can be used with H<sub>2</sub> to form a wide range of hydrocarbons. The Fischer-Tropsch (FT) process is an established method for producing hydrocarbons from syngas: a mixture of CO, H<sub>2</sub> (and sometimes CO<sub>2</sub>). The general formula for the highly exothermic reaction is:



The reaction is generally carried out between 150 and 300 °C and is catalysed by a transition metal such as cobalt or ruthenium at pressures between 1 and 50 atm. FT synthesis is complex, and the exact mechanism is still not known<sup>65</sup>. CO is dissociatively chemisorbed on the catalyst surface and forms CH<sub>x</sub> monomers (where x is between 1 and 3) which then couple to form hydrocarbon chains<sup>65</sup>. These are hydrogenated or dehydrogenated to give either paraffins or olefins. Since the monomer coupling step is uncontrolled, a statistical distribution of products of different carbon numbers is formed. The product distribution follows the Anderson-Schultz-Flory (ASF) distribution:

$$M_n = (1 - \alpha)\alpha^{n-1}$$

Where  $M_n$  is the mole fraction of carbon number  $n$  and  $\alpha$  is the chain growth probability. The reaction conditions can alter the chain growth probability to favour either light or heavy hydrocarbons, but the maximum mole fraction for diesel (C<sub>10</sub> to C<sub>20</sub>) is 39 %<sup>65</sup>. Therefore, significant refining is required to produce liquid fuels.

It is possible to use SOECs to co-electrolyse H<sub>2</sub>O and CO<sub>2</sub> to make syngas, which can then be converted to hydrocarbons via Fischer-Tropsch<sup>66</sup>. Methane, which is a generally unwanted side product, can be recycled back to the anode where it can be oxidised as fuel to reduce the electricity input required to run the SOEC<sup>66</sup>. A recent techno-economic analysis of an integrated process for converting CO<sub>2</sub> and H<sub>2</sub>O to light olefins using a SOEC partially powered by recycled methane found that the largest capital cost was the SOEC at 22 % of the total capital cost, and the largest operational cost was electricity at 63 % of the total operational cost<sup>67</sup>. Sensitivity analysis showed the electricity price to have the highest impact on the levelised cost of the products. Therefore, if renewable electricity prices continue to decline, this process should become more competitive with the fossil route.

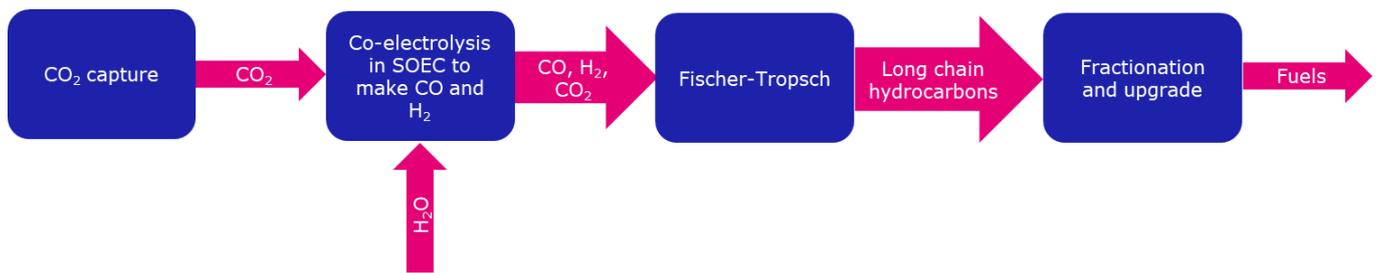


Figure 8: Graphical summary of a process in which CO<sub>2</sub> and water are co-electrolysed to produce syngas, which is then liquified in the Fischer-Tropsch process

A 2018 analysis also predicted that, in the best case, diesel produced by this process could be competitive with fossil-derived diesel by 2037, with most of the cost reductions coming from improvements from learning by doing and scaleup of SOEC<sup>68</sup>.

Compared to the EcoFuel process, this route benefits from the higher TRL of 9 for the Fischer-Tropsch process<sup>69</sup> and the TRL of 6 for SOEC<sup>70</sup>. In comparison, the oligomerisation process in EcoFuel is not currently commercialised and the CO<sub>2</sub> to hydrocarbons electrolysis which is at TRL 2. However, the maturity of Fischer-Tropsch means it is unlikely that large cost reductions can be made in this technology.

Taking the process as a whole, an advantage of this route is that the gas from the SOEC can be fed directly into Fischer-Tropsch with no need for separations, whereas the EcoFuel route requires separation of the different reduction products before the oligomerisation process because contaminants such as CO can deactivate the catalyst<sup>71</sup>. However, the presence of hydrogen may be beneficial in maintaining catalyst activity by limiting the formation of large unsaturated species which are known to deactivate catalysts<sup>71</sup>.

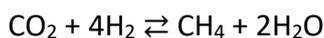
## REVERSE WATER GAS SHIFT AND FISCHER-TROPSCH

The process in the previous section produced syngas for Fischer-Tropsch electrochemically, however the reverse water gas shift (RWGS) reaction is a more established method of producing syngas, which can use hydrogen produced by a water electrolyser powered by renewable electricity.

The formula for the reversible water gas shift reaction is:



The formation of CO is slightly endothermic<sup>72</sup> and a competing reaction is CO<sub>2</sub> methanation, which is highly exothermic<sup>72</sup>.



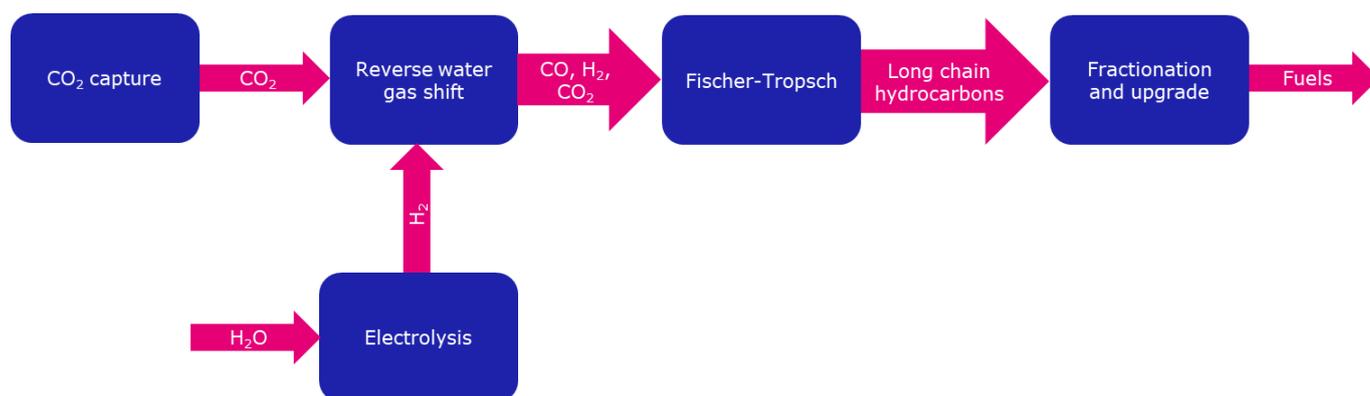


Figure 9: Concept block diagram of a process in which captured CO<sub>2</sub> and H<sub>2</sub> from water electrolysis are converted to syngas by the reverse water gas shift reaction and then converted to hydrocarbons by Fischer-Tropsch

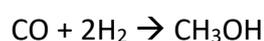
The ratio of H<sub>2</sub> to CO in the feed affects the products made by Fischer-Tropsch: higher H<sub>2</sub>/CO ratios result in a decrease in the production of high molecular weight hydrocarbons and vice versa. Decreasing the ratio increases production of hydrocarbons but increases energy consumption<sup>73</sup> and so it may be desirable to tune the CO to H<sub>2</sub> ratio. This is relatively easy for both RWGS and SOEC as in the former it is possible to increase or decrease the production rate of H<sub>2</sub> from water electrolysis, and in the latter the ratio of CO<sub>2</sub> to H<sub>2</sub>O fed to the electrolyser can be changed.

A recent study compared the energy efficiencies of two hypothetical plants fed with CO<sub>2</sub> from biogas, one of which employed the process depicted in Figure 9 and another which used that of Figure 8, both as energy integrated processes<sup>74</sup>. The RWGS plant used an alkaline water electrolyser as its H<sub>2</sub> source. The total plant energy efficiencies were similar at 81 % for the plant using SOEC and 72 % for the one using RWGS<sup>74</sup>. In 2021, Ordonez *et al*<sup>75</sup> conducted a joint TEA and LCA comparing Fischer-Tropsch plants generating syngas via either RWGS using hydrogen from a PEMWE or by co-electrolysis in a SOEC. They calculated net production costs for the plants, assuming they were situated in the UK, and found the SOEC plant to be 13.0 % more expensive at the current cost of wind electricity of 0.16 \$ kWh<sup>-1</sup> and 6.4 % more expensive if the price of electricity was zero. Even with free electricity, the net production costs of the electrofuels were 1.5 times higher than fossil petrol, meaning a carbon tax of around \$ 200 per ton of CO<sub>2</sub> would be required to make them competitive. The rationale given by the authors for including calculations based on free electricity is that such plants may be used to re-dispatch excess renewable energy.

## METHANOL TO GASOLINE

An alternative to Fischer-Tropsch for the production of hydrocarbons is the methanol to gasoline or MTG process. Of course, before hydrocarbons can be produced from methanol, methanol itself must be synthesised from CO<sub>2</sub>. Most methanol is produced from syngas produced in steam methane reforming, in a process simultaneously involving the CO<sub>2</sub> hydrogenation, CO hydrogenation and the water gas shift reaction.

Starting with CO<sub>2</sub> and H<sub>2</sub> as initial feedstocks there are two options. The first is that CO<sub>2</sub> is converted to CO via RWGS and then CO is hydrogenated to methanol as in the reaction below.



Alternatively, methanol can be directly produced by CO<sub>2</sub> hydrogenation by the following reaction:



The main issues with direct CO<sub>2</sub> hydrogenation is the water it produces and the fact it is accompanied by an undesirable RWGS reaction. However, the reaction using CO is significantly more exothermic (-90.77 kJ mol<sup>-1</sup>) compared to that using CO<sub>2</sub> (-49.16 kJ mol<sup>-1</sup>)<sup>76</sup> which means that more expensive reactor designs, both in terms of capital and operating costs, are required. Of course, cutting out the RWGS step reduces process complexity and requires one fewer reactor. Overall, it appears that for making CO<sub>2</sub> derived fuels, the direct CO<sub>2</sub> hydrogenation is favourable. Indeed since 2011, the George Olah renewable methanol plant in Iceland has recycled thousands of tons of CO<sub>2</sub> per year this way<sup>77</sup>. Therefore, process that will be studied here will produce methanol by CO<sub>2</sub> hydrogenation, the overall process chain for which is shown in Figure 10.

Following methanol production, methanol is reacted over a zeolite catalyst to produce alkanes. This reaction proceeds in two steps. First methanol is partially dehydrated, giving dimethyl ether:



Dimethyl ether is then further dehydrated/polymerised with residual methanol over a zeolite catalyst to give alkanes<sup>78</sup>. It is possible to reduce capital expenditure by using a fluidised bed reactor, rather than a fixed bed reactor, as this allows both the reaction to dimethyl ether and the subsequent hydrocarbon formation reactions to proceed in a single reactor.

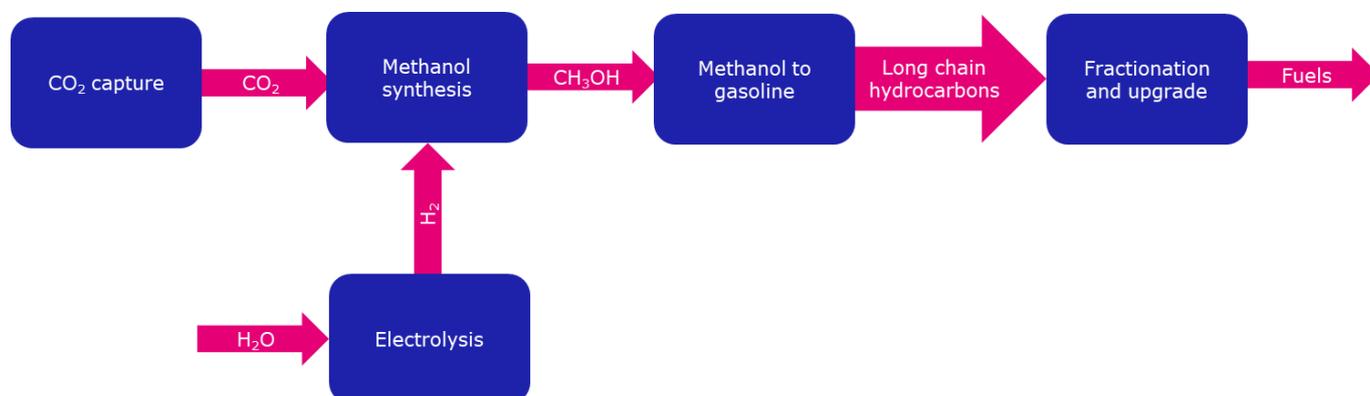


Figure 10: Concept block diagram of a process in which captured CO<sub>2</sub> and H<sub>2</sub> from water electrolysis are first converted to methanol, which is then converted to a mixture of hydrocarbons in the methanol-to-gasoline process

An advantage of this process chain is that the hydrocarbon synthesis step is not constrained by the statistical limits on the selectivity for particular fractions that limit Fischer-Tropsch<sup>79</sup>.

Gasoline produced by MTG has a higher energy demand than FT products when normalised to the lower thermal limit of a diesel equivalent and this is mainly because the heat from FT can be used to run an integrated capture process, such as the one from Climeworks<sup>80</sup>. However, the cost of manufacturing a litre of equivalent diesel (in terms of lower heating value) is lower for MTG, which has a higher power to fuel efficiency. But there is limited value in making gasoline fractions from CO<sub>2</sub> since today's light duty transport such as gasoline powered passenger cars will be relatively easy to directly electrify with batteries compared to shipping and aviation which burn higher C-number hydrocarbons.

Therefore, it is promising that Mobil has achieved conversion of methanol to kerosene and diesel<sup>98</sup>. The process first converts methanol to light olefins, which are then oligomerised, hydrotreated and fractionated. Yields in either the distillate (kerosene and diesel) or gasoline fractions can be as high as 80 %<sup>81</sup>.

In 2018 Schmidt *et al*<sup>98</sup> conducted a techno-economic analysis comparing the production of aviation fuel via the RWGS-FT route discussed above and a route in which methanol was synthesised by CO<sub>2</sub> hydrogenation and then converted to the distillate fraction via Mobil's process and found the methanol pathway to have a very slightly higher overall energy efficiency than the FT route and also a slightly lower cost per litre of aviation fuel produced.

## EMERGING THERMOCATALYTIC ROUTES FROM CO<sub>2</sub> TO FUELS

Recent literature gives a glimpse of new thermocatalytic routes from CO<sub>2</sub> to hydrocarbon fuels with potential benefits over those based on the more established processes detailed above. While no serious techno-economic analysis has been performed on these processes, it is worthwhile briefly considering how they may improve the economic feasibility of sustainable fuels.

In 2017 Wei *et al*<sup>82</sup> reported a multifunctional Na-Fe<sub>3</sub>O<sub>4</sub>/zeolite catalyst which converted CO<sub>2</sub> and H<sub>2</sub> to gasoline range hydrocarbons with 77 % selectivity in a single step. The single catalyst had three types of active site each in close proximity to the other: Fe<sub>3</sub>O<sub>4</sub> sites which catalysed RWGS, Fe<sub>5</sub>C<sub>2</sub> sites for subsequent olefin synthesis from syngas and zeolite acid sites for olefin oligomerisation. While the overall CO<sub>2</sub> conversion was only 22 %, the catalyst showed good stability for 1000 hours in operation. The obvious benefit of this approach is one which many of the processes discussed above share: it condenses several reactions into a single reactor and therefore could significantly reduce capital cost. However, a problem with having three reactions occurring in a single reactor is that it is usually impossible to run all three at their optimum conditions. A similar study in 2020 by Yao *et al*<sup>83</sup> used an Fe-Mn-K catalyst, which gave a 47 % selectivity to hydrocarbons in the aviation fuel range, proving that this catalyst and process design concept can be extended to produce higher hydrocarbons.

Also in 2017, Gao *et al*<sup>84</sup> reported a bi-functional catalyst that produced 78.6 % gasoline range hydrocarbons from CO<sub>2</sub> and H<sub>2</sub> in a single step. The catalyst comprised partially reducible In<sub>2</sub>O<sub>3</sub> and zeolites, with CO<sub>2</sub> being hydrogenated to methanol on the oxygen vacancies of the partially reduced In<sub>2</sub>O<sub>3</sub> and subsequent C-C coupling occurring inside the zeolite pores. The CO<sub>2</sub> conversion was even lower for this study than that achieved by Wei *et al*<sup>82</sup> at only 13.1 %.

## BIOLOGICAL ROUTES TO FUELS

An interesting feature of biofuels is that the steps of energy conversion, CO<sub>2</sub> capture, and reduction happen simultaneously and in the same place during the process of photosynthesis. This makes them challenging to directly compare with the non-biological routes discussed above.

The sustainable production of fuels from biological feedstocks is a very broad industry. There exist many different routes to producing biofuel, each with different environmental, economic, and social implications. Each different route has its own feedstocks and produces different product compounds that have limited and specific uses. As such, commenting on the economic aspects of this technology is difficult.

For example, the fermentation of sugars, for which the feedstock might be sugarcane or corn, mainly produces ethanol and other volatile compounds. These compounds are blended into conventional diesel and gasoline as a way to incorporate renewable fuel into the current market.<sup>85</sup> Agricultural and land-use practices are controversial for their detrimental effects on biodiversity, and using food crops for producing fuels in this way presents a difficult social situation when considering the food shortages in many areas of the world. It's possible that any positive impact of reducing fossil fuel consumption is completely negated by these negative effects.<sup>86</sup> In addition, only so much bio-ethanol can be added to the blend before it begins to significantly impact the stability and energy density of the fuel.<sup>87</sup> Consequently, the produced bioethanol may be more appropriate as a feedstock for further processing.

Current processes are focussed on the production and further processing of key intermediates: sugars, syngas and oils/lipids.<sup>88</sup> Biofuels are also characterised by "generation", which refers to the characteristics of the various feedstocks used, shown in Table 5. To help limit the scope of this section, the processes focussed on are the transesterification and hydro-processing of oils, the Fischer-Tropsch processing of biomass-derived syngas and the alcohol-to-jet process conversion of bio-ethanol derived from sugar fermentation.

Table 5: Feedstocks for biofuel production by generation.

First-generation	Second-generation	Third-generation	Fourth-generation
<ul style="list-style-type: none"> <li>Seed-oil crops (edible), eg. palm, soybean, camelina, sunflower</li> <li>Sugar/starch crops, eg. corn, wheat, sugarcane</li> </ul>	<ul style="list-style-type: none"> <li>Seed-oil crops (non-edible), eg. jatropha, castor</li> <li>Grass crops</li> <li>Wood crops</li> <li>Food and municipal waste</li> </ul>	<ul style="list-style-type: none"> <li>Algae/microalgae</li> </ul>	<ul style="list-style-type: none"> <li>Genetically modified organisms</li> </ul>

Currently, biofuels are blended into conventional fuels at varying ratios depending on the production process and final uses. Aviation fuel, for example, has very strict requirements for energy density and other physical characteristics. Unfortunately, pure bio-aviation fuels have not been approved for use and tend to be blended with conventional fuels up to 50%, but sometimes as low as 10%.<sup>85</sup> This is likely to be the case for any alternative aviation fuel described in this study; it is simply notable here because biofuels are already on the market and currently going through the strict approval processes.

A TEA by L. Tao *et al*<sup>89</sup> examines a variety of different plant oil feedstocks for the following factors: geographic distribution, oil yield, prices, chemical composition, and greenhouse gas emissions. Five plant oil feedstocks were selected for further TEA based on being the most appropriate (in the US) for the production of aviation fuel by hydroprocessing. Hydroprocessing is the general term for a group of processes that produce shorter chain carbon fuels from oils, namely hydrotreating, deoxygenation, isomerization, and hydrocracking. It is worth noting that in this process, hydrocracking of C<sub>15</sub>-C<sub>23</sub> compounds produces a mostly random mixture of shorter hydrocarbon products. Many of these compounds will be less valuable than diesel or jet fuel, and therefore this reduces both the economic



value and yield of specific fuel classes. Other noteworthy aspects to this process are the production of propane during the propane cleave step, and the use of hydrogen as a feedstock. The propane by-product is formed by the hydrogen reduction of glycerol, and can be sold and contribute to revenue. The amount of hydrogen used depends on the degree of saturation of the oils, and so varies between different plant feedstocks.

Overall, it was found that the price of the plant-oil feedstock was the biggest contributor to the cost, and therefore had the greatest effect on the minimum selling price of biofuel. In comparison to the feedstock price, the capital and processing costs were insignificant. The cheapest plant feedstock was found to be jatropha oil, which is an inedible, drought resistant and low resource-using plant. The feedstocks analysed produce between 61-72 % jet fuel as a percentage of the total products, with the rest being a mixture of propane, naphtha, diesel and other residues. A single-point sensitivity analysis on the hydroprocessing process using jatropha oil confirms that the oil feedstock price, as well as plant scale, process efficiency and yields to a lesser extent, have the most significant impact on the minimum selling price of the biofuel product.

More recently, there has been interest in using microalgae as the feedstock for producing biofuel. Microalgae is a non-edible feedstock that can be “farmed” in a more industrial setting, thereby decreasing production costs. Jacob *et al*<sup>90</sup> suggest that, assuming the use of current technology, production costs need to be lowered by 2-3 times current values to become commercially viable. It is suggested that improved energy/carbon balance and process scale-up would aid this. A review by Juneja and Murthy<sup>91</sup> gave a thorough breakdown of the costs of such a process: In contrast to the hydroprocessing of seed oils, the material feedstock costs accounted for only 13% of the total operating costs, which is achievable because most of the major nutrients required for algal growth can be supplied by wastewater and industrial flue gas. A sensitivity analysis revealed that the algal lipid content, nitrogen use and plant scale have the most significant impact on the minimum selling price. This highlights the need for further research into increasing the lipid content of the algae as a way of decreasing costs. The price of biofuel from algae is reported to be in a variable range from \$0.92 to \$42.6 per gallon depending on the process<sup>92</sup>, which would suggest it can be somewhat competitive with conventional fuels. Juneja and Murphy also suggest that biofuel from algae is competitive with other alternative fuel production routes. In contrast, a review by Mazik and Gyarmati<sup>93</sup> concludes that microalgal biofuel is generally not competitive with conventional fossil fuels. It's suggested to be worse than even first-generation biofuels, which are currently more established in the industry. Mazik and Gyarmati also conclude, more generally, that state-support in the form of tax exemptions and subsidies is needed to make biofuel price competitive with conventional fuels. Co-products produced in the refining processes, such as propane, glycerol and other cracking products, are thought to be just as important for profitability as the main fuel product.

In comparison to purely hydroprocessing, which involves hydrogen reduction of the triglycerides, the transesterification process involves the production of fatty acid methyl esters (FAME) using triglycerides and methanol. While FAME biodiesel is often blended into conventional fuel, it is not typically used pure in most use cases due to its degree of unsaturation and oxygen content. For this reason, FAME biofuel is unsuitable as aviation fuel without further processing to saturate the carbon chains, remove oxygen and modify the chain length. This “further processing” would typically be hydrotreating and hydrocracking, which comes under the umbrella term hydroprocessing, as discussed above. The transesterification process for removing glycerol is conducted under milder conditions than equivalent hydrotreatment and propane cleave steps at the cost of additional chemical processing steps later on. A review by J. Marchetti *et al*<sup>94</sup> compares three different transesterification process models (each using different types of catalyst)

and investigates the economic indicators involved. It was found that in two of the three case studies, referring to those that used a homogeneous alkaline catalyst and heterogenous solid-resin catalyst, a positive net present value (7 % interest) was calculated. The heterogeneous catalytic process was the most profitable, owing to the lower initial total investment and slightly higher process efficiency. It is noted that 80+ % of the operating costs comes from the cost of the oil feedstock, making it one of the most significant economic indicators in this process. This seems to be consistent with most oil-derived biofuel processes. This review doesn't consider that further processing would be needed to make this fuel usable for aviation purposes.

A techno-economic analysis by Michailos and Bridgewater<sup>95</sup> evaluated and compared three bio-oil upgrading processes: hydroprocessing, gasification followed by Fischer-Tropsch (G+FT) and zeolite cracking. These three processes are considered types of biomass fast pyrolysis, which refers to the heating of biomass in the absence of oxygen, and are used to convert bio-oil into bio-aviation fuel. In G+FT, the biomass is heated with steam and catalysts to produce syngas. Hydrogen is sometimes added, and the syngas mixture is fed into a Fisher-Tropsch reactor to produce liquid fuels. In zeolite cracking, a zeolite catalyst is used at high temperature to crack the bio-oil into shorter chains, producing fuels.

The feedstock and bio-oil production is kept constant for all three processes, so any differences in technoeconomic viability come from other factors such as yield, energy efficiency, process specific feedstock prices, and other operational and investment costs. In terms of aviation-fuel yield (g/g dry feedstock), hydroprocessing was the most efficient, at 9.79%, followed by G+FT (8.68%) and zeolite cracking (8.14%). This represents a carbon efficiency of 34%, 31% and 30% respectively. In comparison to hydroprocessing, G+FT comprises of more processing steps, so has a lower yield as expected. G+FT also suffers from low single pass conversion of CO in the FT reactor that limits overall CO conversion to 80%. For zeolite cracking, a large portion of the carbon is deposited as coke or released as CO<sub>2</sub>. The hydrogen demand is also a significant cost concern, for which hydroprocessing needs 186.9 kg per tonne of hydrocarbon product, G+FT needs 23.1 and zeolite cracking required none. Overall, hydroprocessing was the most energy efficient (48.8%), followed by G+FT (45.73%) and zeolite cracking (45.38%). It is also worth noting that all three processes are energy autonomous for both heating and electricity, with any excess electricity being sold to the grid. As such, the total energy efficiency is calculated with this in mind.

Finally, the minimum selling price of the jet fuel product was calculated to be 1.98, 2.32 and 2.21 \$/L for the hydroprocessing, G+FT and zeolite cracking respectively, converting to 9.00, 10.55 and 10.05 \$/gal. These prices are 4.8-5.4 times higher than the fossil fuel equivalent. Sensitivity analysis highlighted the biomass feedstock price, moderate scale-up and process efficiency as the most significant ways to decrease the minimum selling price. Michailos and Bridgewater conclude that positive economic return is impossible under the existing circumstances, but that technological advances, policy changes and market advances could move this process towards profit.

Alcohol-to-Jet is (ATJ) is another process for producing bio-aviation fuel. Firstly, alcohols like ethanol and butanol are produced from the fermentation of sugars, starches and/or cellulose. The alcohols are then dehydrated, oligomerised and hydrogenated to produce liquid hydrocarbon products. A stochastic techno-economic study by Yao *et al*<sup>96</sup> determines the net present values and minimum selling prices for the ATJ process using three feedstocks: sugarcane, corn grain and switchgrass. These feedstocks are considered to have different feedstock-to-ethanol conversion factors, based on different processing yields, sugar content and prices, but all share the same ethanol-to-fuel conversion factor. Therefore, any difference in overall yield efficiency is a result of the feedstock itself. In this study, net present values were

presented as distributions, quoting stochastic dominance of each feedstock, with the mean values of the statistical distributions indicating the best feedstocks. It was found that all three feedstocks' probability of loss was higher than 85%, with each giving negative mean net present values. Sugarcane was the best performing feedstock, followed by corn and switchgrass. It is noted that for sugarcane processing, the bagasse (biomass waste) can be used to generate all the heat and electricity needed to power the fuel production and the excess can be sold to the grid for extra revenue. Bagasse burning for the other feedstocks was insufficient to fully power the fuel-making process and so natural gas/electricity would need to be purchased. The mean breakeven jet fuel prices were calculated as 0.96, 1.01 and 1.38 \$/L for sugarcane, corn and switchgrass respectively, converting to 3.65, 3.84 and 5.21 \$/gal. This is lower than the seed-oil-derived bio-aviation fuel discussed above, which suggests alcohol-to-jet is the more viable process right now. However, it still indicates that subsidies and legislative support are needed to make these processes compete directly with conventional aviation fuel.

Bio-fuel could become a valid and profitable process for the development of sustainable fuels in the future. Currently, the price of feedstocks seems to have the biggest impact on profitability, with process efficiency and initial investment costs also being highly impactful. Research into new feedstock sources, like algae and genetically modified organisms, could be the solution. However, the production of bio-fuel needs to be more than just profitable: the impacts of mono-cultured farming practices and land use remain a controversial issue that raise questions on how sustainable bio-fuel production really is. Third-generation, algae-derived biofuel seems to offer the most benefits in terms of decreased land-use and feedstock usage. It may also be the only bio-fuel able to truly approach being carbon-neutral. However, this technology is newer than first and second-generation bio-fuel and, as such, is further behind in terms of plant scale and technology level. Future developments will likely make this a highly competitive option.

## CONCLUSION

In conclusion, there are several economic hurdles that CO<sub>2</sub> derived fuels must overcome to reach large scale commercialisation. On the surface this is an obvious statement since fossil fuels almost completely dominate today's markets, and this is because with today's technologies, economic incentives, and legislation it is more profitable to use fossil hydrocarbons as the source for fuels. As mentioned above, this is partly because fossil fuels pay a relatively low price for their negative externalities i.e., the environmental and health damage they cause, while also benefiting from 480 billion USD in worldwide subsidies in 2021<sup>97</sup>. Fossil fuels' economic advantage is also a consequence of their incumbency: they have been used on a large scale for over one hundred years, which means the processes used to produce them have already benefited from enormous efforts to optimise their efficiency. Furthermore, they benefit from the cost savings associated with their massive economies of scale. Schmidt *et al*<sup>98</sup> point out that Shell's Gas to Liquids facility can produce 14700 equivalent barrels of oil per day, which if made by Power to Liquids would require 3 % of the 2015 German electricity demand to run the water electrolyser alone. This highlights a significant economic hurdle that CO<sub>2</sub> derived fuels face: for plants to reach scales competitive with fossil fuels, very high risk investments must be made. Another fundamental reason it is challenging to compete economically with fossil hydrocarbons is that the energy intensive process of "activating" or reducing carbon has already been completed for fossil fuels, whereas this is an essential step in the production of CO<sub>2</sub> derived fuels. Another way to express this is that fossil fuels are also CO<sub>2</sub> derived, but the CO<sub>2</sub> was captured and reduced by photosynthesis in ancient plants millions of years ago.

Put simply, without changes to legislation, there is no reason to believe CO<sub>2</sub> derived fuels will compete with fossil fuels in the near future. However, as mentioned above, deep decarbonisation of power,

industry and transport as well as negative emissions technologies are essential for avoiding dangerous levels of global warming<sup>38</sup> and so it is likely that future legislation will be designed tip the economic balance toward CO<sub>2</sub> derived fuels and chemicals.

At this time, it is very difficult to assess which route from CO<sub>2</sub> to fuels is most economically competitive. In the course of this review, no published comprehensive assessments of several competing routes were found. The task of calculating the most promising route directly from literature is almost impossible without the construction of a process model taking into account energy and heat integration. Energy efficiencies for individual processes in a chain are often not explicitly quoted and are essentially meaningless due to the large impact heat integration can have on overall efficiencies. A compounding difficulty, as mentioned above, is the large differences in TRL of competing processes. Although an exact quantitative comparison is unfeasible at this stage, comparing processes at today's TRLs simplifies the task of identifying the most favourable.

The conclusion of this report is that, excluding the already commercial biological routes, the most economically attractive route from CO<sub>2</sub> to fuel today appears to be via Fischer-Tropsch synthesis with either the reverse water gas shift reaction or high temperature co-electrolysis of CO<sub>2</sub> and water providing the syngas. More often than not, these routes were found to be more cost effective than competitors and this was largely a consequence of the benefits of integrating heat from the exothermic FT reactor to help heat or power other processes. Today, the most economical source of CO<sub>2</sub> is from point sources, but further technological development and the anticipated tightening of environmental legislation mean direct air capture is also likely to play a significant role in CO<sub>2</sub> supply for fuels.

Promising future routes, which are at present not technologically mature enough for proper assessment, are recently discovered one-step thermocatalytic routes which use multifunctional catalysts to convert CO<sub>2</sub> and H<sub>2</sub> directly to hydrocarbons in the gasoline and aviation fuel range either via Fischer-Tropsch or methanol synthesis mechanisms.

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