

Techno-economic analysis of large-scale production of e-methanol, via CO₂-hydrogenation, in Power-to-X

by

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Picture on front page: AI-generated image by Jonathan Ahlbäck Ikonen using BlueWillow.

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Abstract

Global levels of carbon emissions are constantly rising causing irreversible damages to ecosystems. The heavy transport sector and the industrial sector are responsible for large amounts of the emissions on a yearly basis. Therefore, Power-to-X is presented as an alternative pathway for the production of industry standard chemical, in view of a green transition towards decarbonising emission-heavy sectors. Methanol is one of the desired end-products generated from a multitude of pathways within Power-to-X. Methanol, referred to as e-methanol if produced this way, are synthesised from hydrogen, produced by electrolysis powered from renewable sources, and captured carbon dioxide. Hence highlighting a green production of e-methanol.

This project aims at evaluating different technologies in the production chain of e-methanol in order to do a techno-economic study of a plant configuration capable of producing 46,000 ton/year of e-methanol via green hydrogen and captured carbon dioxide. The technical evaluation showed that the best suited technologies for an e-methanol plant of this scale and configuration were hydrogen produced via a PEM electrolyser, compressed via mechanical multistage compressors, and distributed to a methanol synthesis plant together with carbon dioxide captured via amine-based absorption. A comprehensive simulation model of the methanol synthesis loop was developed with support of Aspen Plus, whilst the other process steps were estimated in a detailed economic analysis – with a basis in the capital- and operational cost associated with a large-scale commercialised e-methanol plant with an expected lifetime of 20 years of operation. The economic analysis showed that the levelized cost of methanol (LCoM) was 1041 €/ton, which is more than double the current market value price of methanol (400 €/ton). Additionally, the analysis showed that the net present value (NPV) of the e-methanol plant was negative 297 M€, if methanol was sold at the current market value, at the end of the project lifetime. The sensitivity analysis showed that electrical power consumption per produced kilogram of hydrogen and the current industrial price of electricity, had the largest effect on the NPV. However, a futuristic scenario was analysed where four parameters were changed based on forecasted values. This analysis showed that e-methanol production could become significantly profitable with a NPV of 111 M€ after the project lifetime. Hence justifying the growing interest of e-methanol production.

Populärvetenskaplig sammanfattning

Den ökande globala temperaturen och dess förödande irreversibla effekter på jordens ekosystem är en av mänsklighetens största utmaningar. Den största bidragande faktorn till temperaturökningen är våra ökande utsläpp av växthusgaser, såsom koldioxid, och andra föroreningar. Metrologiska världsorganisationen har estimerat att vi kommer accelerera förbi en temperaturökning på 3 °C år 2100, om vi fortsätter denna ökning av koldioxidutsläpp. Detta skulle innebära total planetär kris och vi skulle mest troligt få bevittna ett massutdöende av miljardtals livsformer här på planeten. Trots den stora utmaningen som vi alla står inför så säger generalsekreteraren för Förenta nationerna, António Guterres, följande i ett uttalande “the climate emergency is a race we are losing, but it is a race we can win”. I dagsläget kommersialiseras teknologier som är ämnade att minska eller neutralisera utsläppen av koldioxid inom flertalet industrier. I dagsläget kommer majoriteten av de globala koldioxidutsläppen från energi-, industri- eller transportsektorn där fossilbaserade alternativ används. För att minimera påverkan och bromsa effekterna på klimatet är det därför nödvändigt att övergå till mer hållbara och grönare alternativ för energi-, material- och drivmedelsproduktion.

I denna studie presenteras Power-to-X som en lovande lösning för en sådan övergång, mer specifikt för en grönare produktion av metanol, benämns som e-metanol i denna bemärkelse. Metanol är en av världens mest producerade kemikalier och används som drivmedel inom den tunga transportsektorn och inom många processer inom läkemedels- och tillverkningsindustrin. Inom produktionen av e-metanol används teknologier för att producera energi från förnybara resurser som sedan används för att producera vätgas. Vätgasen, tillsammans med infångad koldioxid från rökgaserna som lämnar ett kraftverk, används sedan som reaktanter i en reaktor som producerar e-metanol. Processen är teoretiskt helt grön då överskottsenergi från gröna källor samt infångad koldioxid neutraliserar koldioxid avtrycket på klimatet.

Målet med arbetet var att undersöka om en storskalig produktion av e-metanol är ekonomiskt lönsam i dagsläget såväl som i framtiden för att kunna påvisa investeringsmöjligheter som skulle påskynda utvecklingen- och avancemanget av kommersialiseringen av teknologierna.

Resultaten visade att man i dagsläget skulle behöva sälja e-metanol för mer än ett dubbelt så högt pris som konventionell metanol producerad från fossila källor. Om e-metanolen skulle säljas för samma marknadsvärde som fossil-baserad metanol, skulle den ackumulerade kostanden, efter 20 år av produktion för en sådan e-metanolfabrik, vara 296 M€. Resultaten visade också att en sådan e-metanolfabrik skulle visa sig vara extrem lönsam i framtiden baserat på hårdare policys av koldioxid-utsläpp, förbättrad effektivitet, lägre elpris och växande efterfrågan av metanol. Detta bidrar till att en framtida e-metanolfabrik uppskattningsvis skulle generera en inkomst på 111 M€ efter en operativ period på 20 år.

Abbreviations and Symbols

AWE	Alkaline Water Electrolysis
BEC	Bare Erected Cost
CAP	Chilled Ammonia Process
CAPEX	Capital Expenditure
CCS	Carbon Capture & Storage
CCUS	Carbon Capture Utilisation & Storage
CO ₂ e	Carbon Dioxide Equivalents
DME	Dimethyl Ether
HER	Hydrogen Evolution Reaction
KS-1	
LCOHs	Liquid Organic Hydrogen Carriers
LCoM	Levelized Cost of Methanol
LHHW	Langmuir-Hinshelwood/Hougen-Watson
MEA	Monomethanolamine
MEA*	Membrane Electrode Assembly
NPV	Net Present Value
NREL	National Renewable Energy Laboratory
OER	Oxygen Evolution Reaction
OPEX	Operational Expenditures
P2F	Power-to-Fuels
P2X	Power-to-X
PEC	Purchase Equipment Cost
PEM	Proton Exchange Membrane Electrolyser
PtX	Power-to-X
RWGS	Reverse Water Gas Shift
SAF	Sustainable Aviation Fuel
SOEC	Solid Oxide Electrolyser
TEA	Techno-Economic Analysis
TRL	Technical Readiness Level
WACC	Weighted Average Cost of Capital
WHO	World Health Organisation
WMO	World Meteorological Organisation
YSZ	Yttria-Stabilised Zirconia

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1. Introduction

The climate crisis is one of the most concerning crises of our time and it is happening at such an accelerating rate that some of the damages caused on global ecosystems are irreversible. The increased global temperature is the concern and has a great bearing on the matter at hand. According to the World Meteorological Organisation (WMO) we have surpassed levels of one degree Celsius above that of pre-industrial temperatures and alarming indications suggest that we are nowhere near decelerating our yearly global emissions of greenhouse gases¹. The global emissions of greenhouse gases (measured in carbon dioxide equivalents, denoted CO₂e) are increasing on a yearly basis². With the current trajectory of our global emissions, it is estimated that we will end up far beyond a 3-degree Celsius increase around year 2100 which would have catastrophic consequences for the survival of billions of species on our planet including humans. This crisis is described as a race of survival for life on this planet and as pointed out by the UN's General Secretary António Guterres "the climate emergency is a race we are losing, but it is a race we can win"¹.

The majority of global emissions of carbon dioxide resides from the electricity and heat sector, followed by the transport sector as well as the industrial sector. The transition from fossil-based derivatives to renewable energy, within these three sectors, is therefore identified as essential in achieving decreased emissions. There are several emerging new technologies that utilise renewable energy, such as wind-, water- and photovoltaic power, which is under rapid development. These technologies of renewable energy, coupled with decreasing prices for sustainable and renewable electricity, bear great importance for the competitiveness with fossil-based electricity³. The best available technologies deliver promising results that contribute towards the achievement of making renewable energy cheaper. However, further development and innovation regarding technologies are essential for this transition towards more affordable and renewable energy. Thorough persuasive techno-economic assessments of technologies, involving improved efficiencies in hydrogen electrolysis, fuel production, compression as well as transportation and storage, are required to fully convince global industrial participation in this transition. A major problem with mature technologies on the market today is their inefficiency or high capital- and operational costs in comparison to fossil-based alternatives.

Power-to-X (P2X or PtX) is an emerging technological process involving green hydrogen production and carbon capture utilisation in order to synthesise fossil-free alternatives. In other words, P2X is the concept of converting renewable energy ("Power") to a product ("X"), which would otherwise be produced from fossil sources. This is one of the main contributing factors for the increased interest in the P2X-concept and advancing development of technologies involved. One P2X pathway that has gained interest is the Power-to-methanol producing so called "e-methanol". E-methanol has the potential of a green alternative to fossil-based fuels and precursors in the heavy transport sector and the chemical industry, thereby reducing the carbon emissions of these sectors.

As an effect of the rising interest in P2X, this thesis aims at providing further knowledge of the benefits of e-methanol production and increase understanding of the techno-economic challenges of e-methanol production via the use of renewable energy sources. The thesis also aims at providing a foundation for further projects designated to increase

the efficiency of operational units within the P2X process chain as well as give further insight into large-scale production of e-methanol. The scale of the e-methanol plant investigated in this techno-economic analysis (TEA) is 46,000 ton/year.

1.1 Problem Definition

The current technologies of e-methanol production coupled with the availability- and price of electricity are relatively far from competitive in comparison with the price of fossil-based alternatives for fuels. According to a detailed study by International Energy Agency, the current price for near-term e-methanol production cost somewhere between 120–210 USD/MWh. However, according to the same study, the long-term production cost of e-methanol are expected to decrease to 55-70 USD/MWh making it competitive with fossil-based fuels which are predicted to experience an increase in production costs due to further significant restrictions of CO₂ emissions⁴. In order to achieve competitiveness with the fossil-based fuels, continuous improvement of many parts of the e-methanol production chain is needed. Optimisation and up-scaling of green electricity production from example wind- and solar power coupled with improvements of distribution- and transportation systems, as well as reformation of electric grids to support P2X processes. Furthermore, advancements in new- or optimisations of best available technologies in the production chain of e-methanol as well as cheaper electricity are necessary for competitive achievement⁵. The long-term decrease in production costs of e-methanol is directly linked with the cost of electricity which contributes to between 40-70% of the total production cost of e-methanol⁵. One of the largest costs of e-methanol production comes from the electrolysis of water into hydrogen. A proton-exchange membrane water electrolyser (PEM), one of the most commonly used technologies for hydrogen electrolysis, accounts for more than 50% of the total bare erected costs (BEC) of e-methanol production⁵. PEM uses technologies which are under rapid advancement and these types of electrolysers are starting to be widely commercialised in the industry sector. The upscaling in production capacity of e-methanol from direct CO₂-hydrogenation is dependent on more efficient operations in combination with favourable site synergies that can lower the production costs, hence making prices more competitive. Therefore, this techno-economic thesis strives at assessing large scale production (46,000 ton/year) of e-methanol and present a feasibility analysis of large capacity plants in order to promote a green energy- and fuel transition.

1.2 Project Scope

The thesis aims at understanding the production chain of e-methanol production and evaluate different parts of the chain in terms of efficiency and best available technology. With the ultimate aim of justifying e-methanol over fossil-based methanol by investigating best available technologies of a large-scale production of e-methanol, via direct CO₂-hydrogenation. The methanol synthesis loop is to be simulated in Aspen Plus whilst other parts of the e-methanol production chain are to be estimated in order to analyse the feasibility of an e-methanol production. To conclude the feasibility of an e-methanol plant of this scale and configuration, a present and a futuristic scenario analysis is conducted to financially justify e-methanol over fossil-based methanol in a near- and long-term perspective.

1.3 Method of approach

The project was approached by a literature study of the different technologies involved in production chain of e-methanol. Thus, increasing understanding of different technologies and evaluating their technological readiness level (TRL), as well as their advantages and disadvantages. This enabled a qualitative evaluation of best method of approach for the design of an e-methanol plant of set scale and configuration. Furthermore, the project involved evaluation of chosen technology in terms of process design, technical data and process modelling and simulation in Aspen Plus, until convergence was reached. The quantitative energy analysis from the methanol synthesis, coupled with the capital- and operational cost estimations of other technologies, together with revenues generated from the projects estimated lifetime of operation was analysed to conclude feasibility. Finally, the performance of the designed process was evaluated, and a sensitivity analysis was conducted. The workflow of this thesis is illustrated in Figure 1.

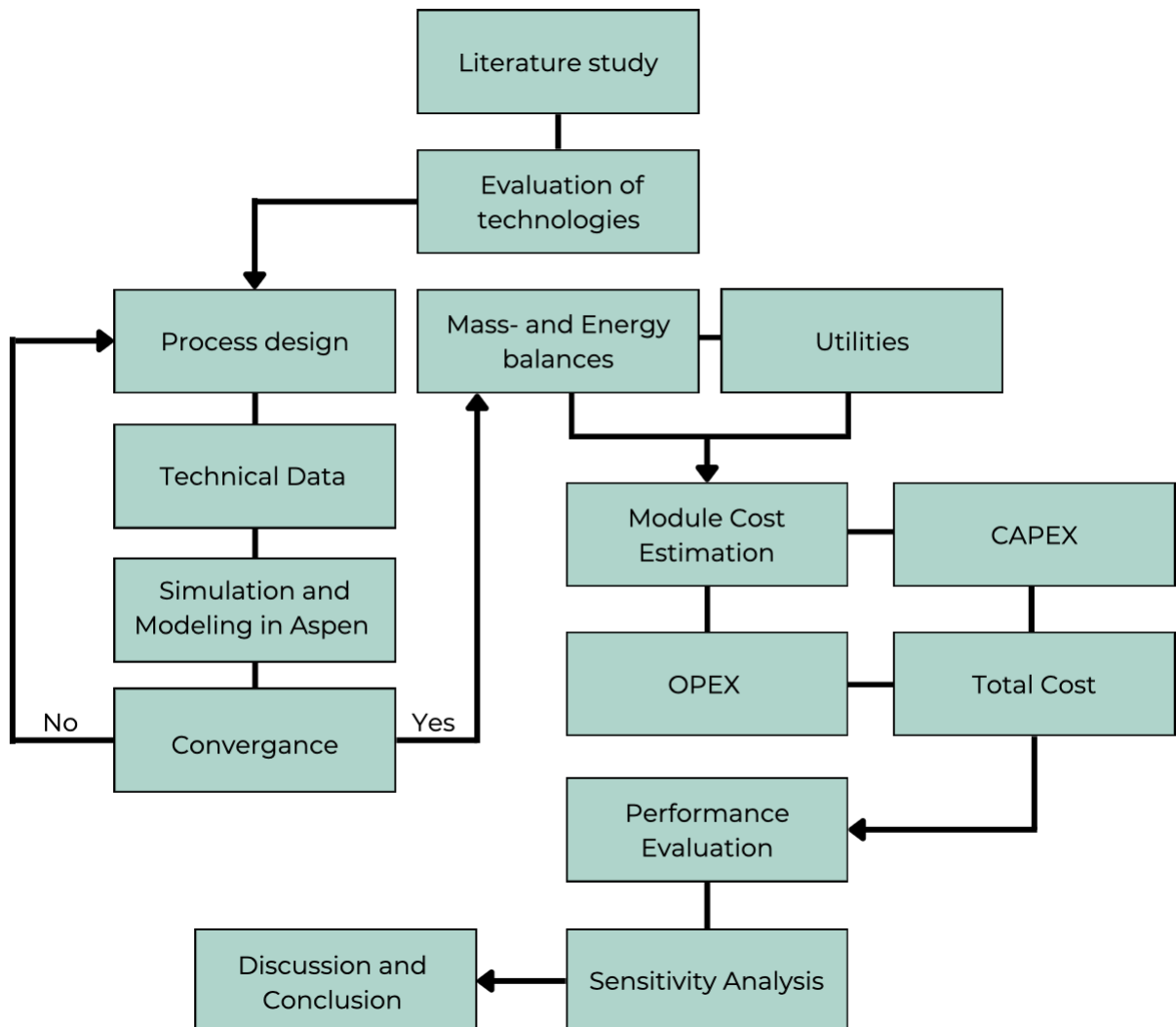


Figure 1: The overall workflow of the thesis.

1.3.1 Project Limitations

There following limitations were set for this:

- Only the methanol synthesis loop was simulated in Aspen Plus. The other parts (electrolysis, compression, and carbon capture) will be based on estimations and models from literature.
- The designed e-methanol plant will have all supporting facilities (electrolysis, compression systems, and carbon capture systems) on site. However, the distribution and transport of hydrogen for potential off-site production will be discussed briefly and evaluated from a technological perspective.
- The availability of electricity was assumed, and technologies of electricity production was not evaluated in this project.
- Legislations and policies involving carbon emissions, except carbon emission credits, was not taken into considerations in this project.
- No results were based on estimations made from synergetic system integrations, such as heat integration with other plants. Only discuss potential improvements. Neither was optimal location of plant considered for the e-methanol production.
- Electricity prices was assumed and did not take location of plant into consideration.
- Financial assumptions were made. However, the assumptions only included inflation and interest rates. Excluding parameters such as working capital, debt, equity etc. for cost analysis and feasibility.
- Transportation and distribution of produced methanol will not be considered. Therefore, it was assumed that the produced methanol was directly sold when leaving the methanol plant.
- The specific needs and materials for pipelines, especially pipelines handling hydrogen, was not considered.

2 Theoretical Background & Literature Review

A problem with renewable electricity is the difficult integration into the power grid due to the intermittent nature of many renewable energy sources such as solar- and wind power³. On the other hand, the energy consumption of our current fossil-based energy system is not fully supported by the power sector which also relies heavily on chemicals and fuels for heat, transport, and industrial processes. This indicates great need for converting and storing renewable electricity in suitable forms to fully transition to an energy system with power originating from 100% renewable resources. This is the very foundation Power-to-X, which strives towards providing renewable energy converted into suitable energy-bearing molecules.

P2X is a broad term and covers a bundle of different pathways for the conversion and storage of electric power where power can be converted to molecules, hence the “X” in Power-to-X, including hydrogen, syngas or for example synthetic fuels (e-fuels), such as e-methanol.

The transport sector contributes to a large share of the global emissions and additionally, it contributes to a third of the final energy consumption in EU. Other energy sectors have successfully managed to reduce their CO₂-emissions during the last couple of years whilst the transport sector, in these terms, are laggards. This is an effect of the ever-growing demand for transportation and the continued dominance of fossil-based fuels. More efficient pathways in the production of e-fuels are needed and the literature suggests that P2X, to some extent, has been hindered in its development due to strict regulatory frameworks, low incentives as well as the uncertainty of future market demand and electricity costs which are indicators of unattractive business cases⁶. However, the demand for sustainable solutions in the “hard-to-abate” sectors (such as industry and heavy transport) and the strive to accomplish net-zero emissions under certain time frames set by the EU commission, increases demand in the industry of P2X and especially in Power-to-fuels (P2F)⁵.

2.1 Overall E-Methanol Process

The current best available process-technologies used in e-methanol production, in the Power-to-methanol process chain, include five major process segments, see Figure 2. Green hydrogen production, via electrolysis, powered by renewable sources of energy. Followed by compression, of both produced hydrogen and captured carbon dioxide, for distribution and storage. Finally, hydrogen and carbon dioxide are fed to a reactor producing the methanol.

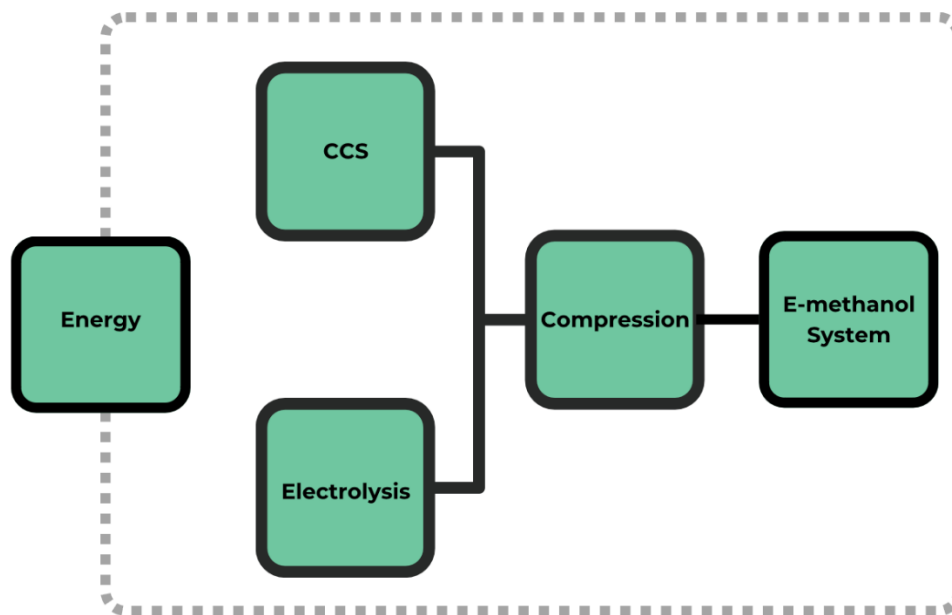


Figure 2: An overall process view of the five major segments in the process chain of e-methanol production.

Some of the attractive pathways of P2X involve synthesis e-fuels such as e-methanol and sustainable aviation fuel (SAF). Both e-fuels are substitute for fossil-based derivatives in the

transport sector. Not only have e-methanol, the main subject of this thesis, applications as e-fuels but also in other industries as it is one of the world's most important chemicals. It is a fundamental building block and precursor in the chemical- and pharmaceutical industry. Furthermore, it is also heavily used in the production of hydrocarbons⁵. The production chain of e-methanol and the combustion of e-methanol as an e-fuel has, theoretically, a net-zero carbon footprint if renewable sources of energy are used to power the operating units throughout the process chain, see Figure 3.

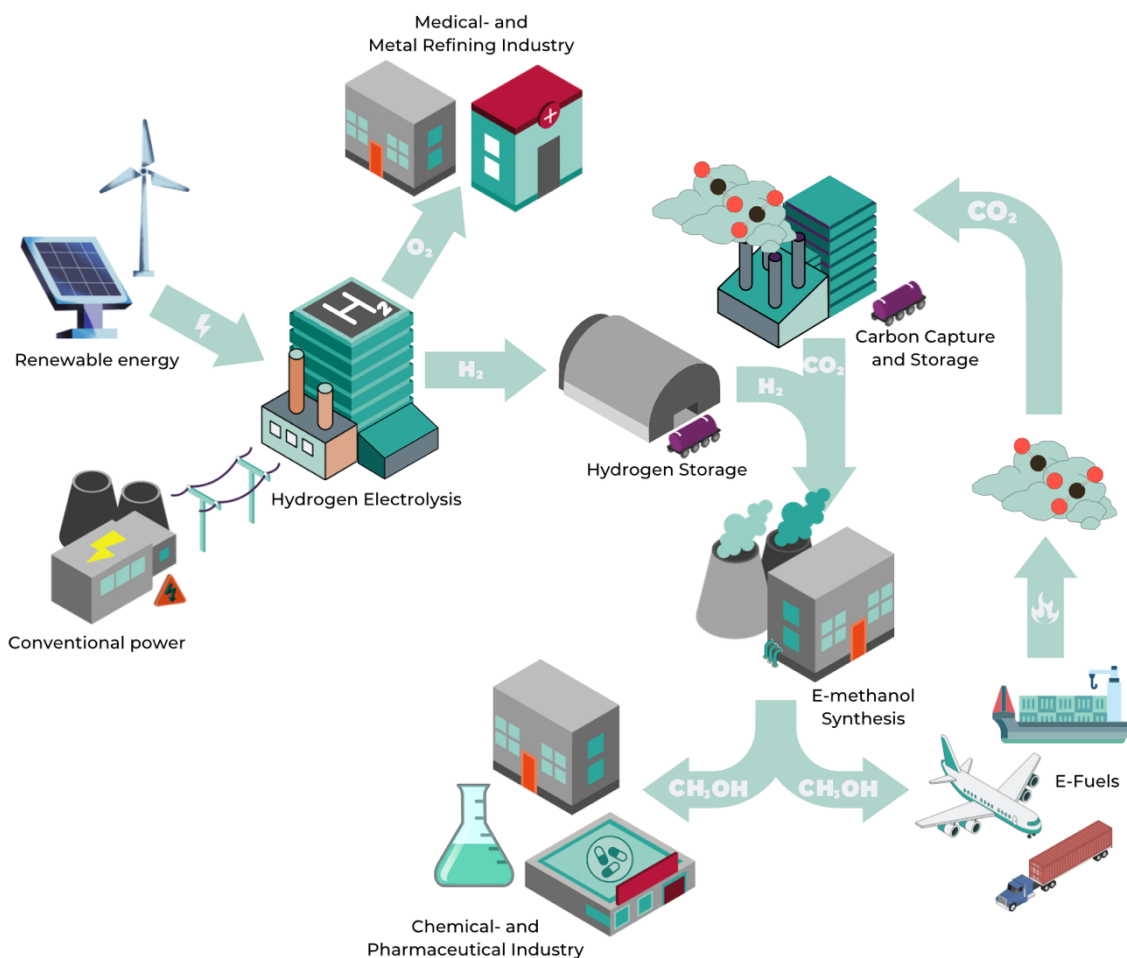


Figure 3: A schematic representation of the Power-to-Methanol pathway where hydrogen, produced via electrolysis, is distributed and stored before methanol synthesis together with carbon dioxide, into e-fuels and precursor for chemical- and pharmaceutical industries. The co-produced oxygen from the electrolysis is distributed to medical- and metal refining industries. Showcasing a net zero carbon footprint if renewable electricity is used in the process chain.

The world's currently largest commercialised plant for production of e-methanol started production in 2022, in Anyang, Henen Province, China. With an annual capacity to produce 110,000 tons of methanol from green hydrogen and captured carbon dioxide⁷. Another e-methanol project, this time, regarding Denmark-based European Energy is currently under construction. The plant is under development and will be located in Kassø, in the southern parts of Denmark. The plant-production of e-methanol will be provided with green hydrogen from a

50 MW electrolyser facility with a large integrated solar power-driven grid network. The plant stands to start production in 2023 and will be the largest e-methanol production plant worldwide⁸. Further indicating increased global interest for production of e-methanol and towards the necessary transition from fossil-based derivatives to renewable recourses. In the case of methanol, the yearly global production of methanol is about 90 million tons and the majority of the produced methanol (roughly 65%) originates from natural gas by means of methane steam reforming processes and the rest (35%) originates from coal, and more specifically from gasification processes⁵. The overall global contribution of produced methanol from green hydrogen is currently neglectable in comparison to other processes. Less than 0.2 million tons (around 0.2% of the total methanol production globally) of produced green methanol are produced on a current yearly basis⁵. However, increasing interest and advancements of promising technologies will most certainly contribute to increased production in the near future.

2.2 Electrolysis

Electrolysis is a technique used in smaller scale chemistry and larger scale industries often to produce a metal from solutions of salts or to purify metals. In P2X, purpose of electrolysis is to split water into hydrogen- and oxygen gas. Electrolysis is a type of redox reaction and involve the transfer of electrons between electrodes, referred to as anode and cathode. Electrolysis of water has a positive value of Gibbs free energy, and consequently are non-spontaneous, hence the use of an added electrical current to drive the reaction is needed. The redox reaction in electrolysis occurs within a unit referred to as an electrolytic cell. Electrolytic cells are different from galvanic cells. In electrolytic cells the electrodes share the same compartment and therefore the same solution of electrolyte. At the anode of an electrolytic cell is here the oxidation reaction is taking place and it is indicated with a plus sign whilst the cathode, indicated with a minus sign, is where the reduction reaction is taking place. The plus sign indicates that the electrode is pulling electrons away from the species of oxidation⁹.

In P2X the electrolysis takes place inside different types of electrolytic cells and the redox reaction involves the splitting of water into hydrogen and oxygen with applied potential through an electrolyte, see Reaction 1.



In this reaction, the electrodes are linked via an applied external electric power supply^{9, 10}. There are three main electrolytic cells available that utilises different technologies in electrolysis of water: proton-exchange membranes (PEM), alkaline water electrolysis (AWE) and solid oxide electrolysis cells. The different cell types are associated with the corresponding technique used for the electrolysis hence, the intermediate reactions are different. However, the overall total reaction is consistent throughout the choice of method^{9, 11}, see Figure 4.

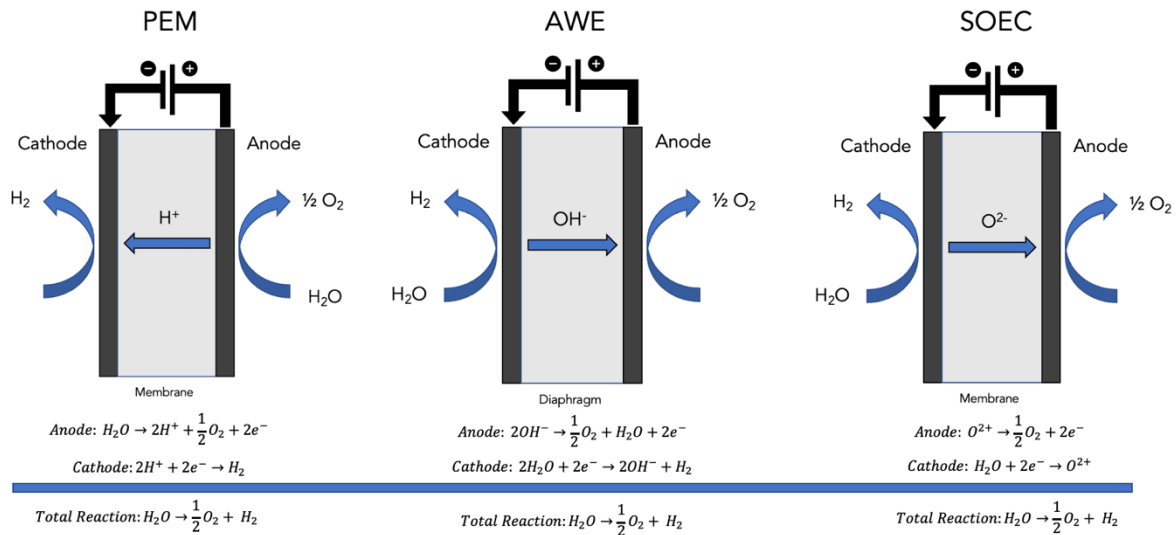


Figure 4: An overall view of the three types of electrolytic cells evaluated in this project. Inspired by the work of Jang, D.; Kim, J.; Kim, D.; Han, W.-B.; Kang, S. *Techno-economic analysis and Monte Carlo simulation of green hydrogen production technology through various water electrolysis technologies. Energy Conversion and Management* 2022, 258, Article. DOI: 10.1016/j.enconman.2022.115499 From EBSCOhost ScienceDirect.

Electrolysis of water in hydrogen production requires large amounts of electricity. One of the contributing factors for the electricity demand in the electrolyser, originates from the positive value of Gibbs free energy for the overall reaction of hydrogen production.

The change in Gibbs free energy is in relation to the change in enthalpy and the change in entropy, see Reaction 2. The overall endothermic reaction has a value of the change in Gibbs free energy of +237 kJ/mole of produced hydrogen, at 25 °C and at standard conditions^{10, 12}. To overcome this value in Gibbs free energy and push the reaction in a reverse direction, opposite to the direction of the spontaneous reaction, the minimal potential required to achieve this is 1,23eV at standard conditions. Therefore, it is desirable to apply an overpotential which is the difference between the standard potential and the actual potential applied. An overpotential is applied to push the reaction in a direction opposite of the direction of the natural pushing power⁹.

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

In the oxygen evolution reaction (OER) at the anode is kinetically sluggish due to energy accumulation in several multi-step reactions thus requiring a higher overpotential whilst the hydrogen evolution reaction (HER) at the cathode is kinetically fast and therefore needs less overpotential^{10, 12}. Much of the current research regarding electrolysis of hydrogen production involve optimising efficiencies by decreasing the amount over potential needed to produce significant rates of production⁹. Other factors taken into consideration when analysing the efficiency of electrolysis are increased temperatures, increased pressures, and the use of catalysts to overcome the kinetic boundaries^{12, 13}.

In this project, three different industry dominated types of electrolysis are analysed and evaluated based on factors such as performance, integration opportunities, technological readiness level etc.

2.2.1 Proton Exchange Membrane

A proton exchange membrane (PEM) cell uses a very thin (usually 100-200 micrometre thick) solid proton-conductive polymer membrane as electrolyte and these types of electrolytic cells are often very compact and small in comparison to other cell types. It is within the very centre of the cell that the electrolysis of water into hydrogen occurs, and this part of the cell is referred to as the membrane electrode assembly (MEA*). The MEA* consists of the conductive membrane in between the two catalytic layers. The catalytic layers consist of a mixture of catalytic particles that are embedded in polymer chains that is often induced with additives to increase the electric conductivity. The catalytic layers are also often porous in order to facilitate away produced gas to decrease the accumulation of produced gas on the reaction sites which increases the osmotic resistance. These accumulated bubbles of gas tend to form resistive gaseous films and these sophisticated mass-transport structures and pores are often very expensive¹⁴.

During the process of water electrolysis, liquid water is oxidised into molecular oxygen at the anode as described in Reaction 3.



The protons and the electrons travel to the cathode where the reduction of the protons takes place described in Reaction 4.



In the catalytic layers at the anode- and at the cathode sections of the unit cell, catalyst particles of platinum respectively iridium particles or IrO₂ is used to lower activation energies and overcome kinetic barriers in the redox reactions¹⁴. A PEM electrolyser typically operates at a temperature range of 50 – 80 °C and at pressures of 200 bar¹¹.

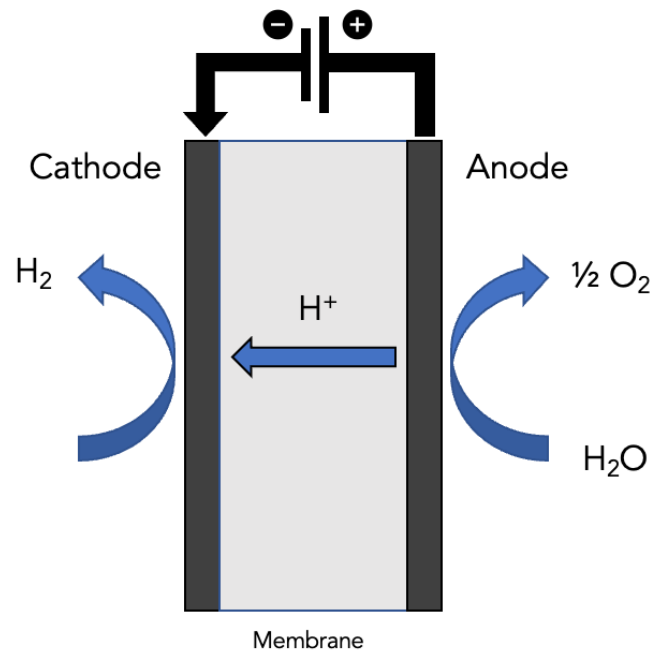


Figure 5: The PEM electrolytic cell. Inspired by the work of Jang, D.; Kim, J.; Kim, D.; Han, W.-B.; Kang, S. *Techno-economic analysis and Monte Carlo simulation of green hydrogen production technology through various water electrolysis technologies. Energy Conversion and Management* 2022, 258, Article. DOI: 10.1016/j.enconman.2022.115499 From EBSCOhost ScienceDirect.

2.2.2 Alkaline Water Electrolyser

In an alkaline water electrolyser, the electrodes are separated by a porous diaphragm with a specific pore size, typically the pores have an average pore size less than 1 micrometre, in order to only be permeable to the hydroxide ions. The diaphragm is fabricated of a structure of ceramic oxides, polymers, glass reinforced polyethylene sulphide with layers of nickel oxide on meshes of various titanium oxides. The electrolytes consist of KOH or NaOH of roughly 20 – 30%. The alkaline water electrolysis process differs from the rest due to the consumption of alkaline solution and additional solution continuously needs to be fed to the electrolytic cell. Furthermore, large variations of catalysts could be used for the OER and HER¹⁰.

The following oxidation reaction occurs at the anode:



At the cathode, the following redox reaction occurs:



An alkaline water electrolyser (AWE) typically operates at temperatures of 60 – 80 °C and at pressures under 30 bar¹¹.

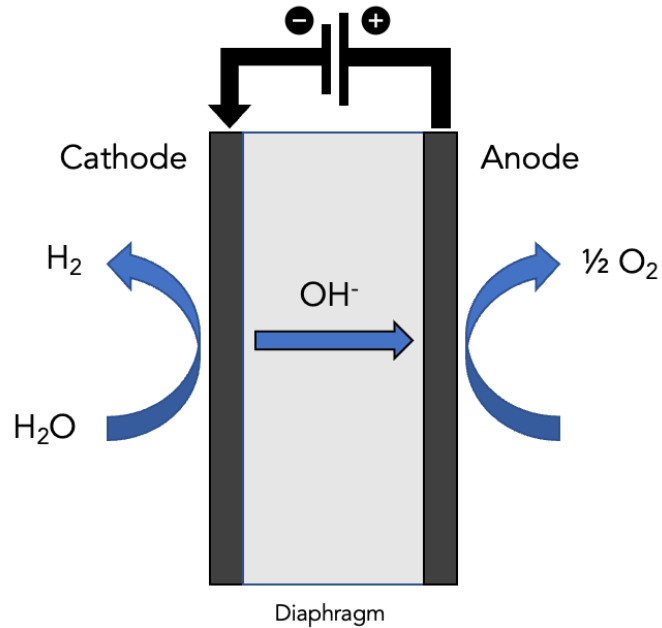


Figure 6: The alkaline electrolytic cell. Inspired by the work of Jang, D.; Kim, J.; Kim, D.; Han, W.-B.; Kang, S. *Techno-economic analysis and Monte Carlo simulation of green hydrogen production technology through various water electrolysis technologies. Energy Conversion and Management* 2022, 258, Article. DOI: 10.1016/j.enconman.2022.115499 From EBSCOhost ScienceDirect.

2.2.3 Solid Oxide Electrolysis

In solid oxide electrolysis (SOEC) a ceramic membrane of yttria-stabilised zirconia (YSZ) is used, to separate the anode and the cathode. YSZ is a very thermoresistant material and enabling process to be operated at very high temperature, 600 – 1000 °C, which contributes to less energy needed to split water. Consequently, in order to maintain high efficiency, the process requires vast amounts of heat to maintain high temperature levels.

The following oxidation reaction occurs at the anode:



At the cathode, the following redox reaction occurs:



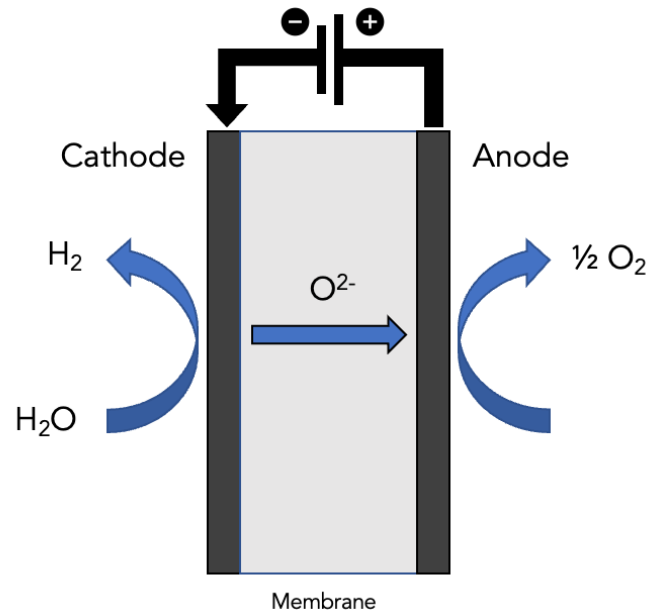


Figure 7: The alkaline electrolytic cell. Inspired by the work of Jang, D.; Kim, J.; Kim, D.; Han, W.-B.; Kang, S. *Techno-economic analysis and Monte Carlo 3 of green hydrogen production technology through various water electrolysis technologies. Energy Conversion and Management* 2022, 258, Article. DOI: 10.1016/j.enconman.2022.115499 From EBSCOhost ScienceDirect.

2.2.4 Evaluation

Advantage with the alkaline method is that it has high durability and do not require novel catalyst, as PEM that for example uses platinum or iridium as catalyst. The capital cost of an alkaline electrolyser is estimated to be in the range of 1000 – 5000 dollar/kW depending on capacity of production¹⁵. Alkaline electrolysis has a high TRL and are the electrolysers most used in commercial plants. Therefore, decreased production cost of hydrogen, in combination with, the maturity of the process makes it a solid alternative for large scale hydrogen production. However, the permeability of the diaphragm allows built up bubbles of produced gas to crossover which creates resistance and decreased efficiency as well as decreased purity of produced hydrogen. Another problem is that the system itself is not very flexible, with long start-up times, which makes integration of renewable energy sources difficult due to the slow response of intermittent input. Thus, interest tends to be oriented towards models with more dynamic operation.

PEM electrolysers are flexible and can operate under fluctuating power supply. This is an advantage considering the use of wind- and solar energy as power supply to the electrolysis due to their intermittent power supply. This is not the case for alkaline electrolysers due to the inertia in ionic transport in the liquid electrolytes with fluctuating power supply¹⁵. The alkaline electrolyser is also in need of continues control of pressure via valves due to the influence of specific gravity of the alkaline solution that constantly is being replenished as the electrolyser operates. The alkaline electrolyser can only operate at a set pressure and needs to be gradually pressurised prolonging start-up times of up to 1 hour¹⁶. This is not the case for PEM electrolysers which can have an immediate to 15 min start-up. Other advantages of the PEM electrolyser, compared to alkaline electrolysers, is that it can operate at lower cell voltage, higher current hydrogen densities, higher temperatures, and pressures which in turn increases efficiency. However, the estimated lifetime of PEM electrolytic cells is shorter due to stack degradation which increases maintenance costs⁵. Due to the use of rare novel metals, such as

platinum and iridium, as heterogenous catalysts the capital costs for PEM are high. However, usage of palladium or homogenous catalyst with turnover rates of 2.4 per mole hydrogen per mole catalyst and second can also be considered in order to decrease costs. Electrolysers are highly sensitive to impurities in the water, especially PEM electrolysers. Hence, desalination and demineralisation is an essential pre-treatment step before electrolysis¹⁷.

SOEC is an electrolyser that shows great energy efficiencies due to its high operating temperatures which reduces energy needed for the decomposing of water. However, the process requires a lot of energy to be able to create- and maintain a high-temperature environment inside the electrolytic cells¹¹. Worth considering is the promotion of degradation phenomenon of the ceramic materials at such high temperatures which add complexity to the method¹³. This indicates that the process needs a consistent heat- and power supply and thus may be unsuitable for integration with renewable electricity sources. This technology is the most immature, amongst previously mentioned technologies, and is not yet commercialised which could make it difficult for integration with large-scale production of hydrogen.

Due to the high technical readiness level of PEM water electrolysis and the flexibility in response to fluctuating power input that could vary the production of hydrogen, this technology is best suited for large-scale production of e-methanol from green hydrogen and clean carbon sources when the electricity flux is high. The technology also provides easier means of maintenance with fewer components in the system. However, the downside being the expected shorter lifetime and high capital cost of equipment and replacement of stack.

2.3 Compression

Compression of hydrogen and carbon dioxide is a crucial step of the production chain of e-methanol. The compression of these feedstocks is necessary for the distribution, transportation, and storage for both centralised- and decentralised e-methanol production. Hydrogen is often compressed under high pressures of 200 – 700 bar, and occasionally compressed and cooled to a liquid. Carbon dioxide is often compressed to a liquid for the storage and distribution. Improvements in hydrogen compression is greatly factorial in the transition to renewable energy. The current commercialised compression of hydrogen requires vast amounts of energy and new technologies are required in order to optimise and overcome present barriers that contributes to higher total costs for produced gases and e-fuels. Compressors contributes to around 20% BEC of an e-methanol plant⁵. This has led to increasing interests in the development of high-pressure electrolysers since the energy required to generate hydrogen with post-pressurisation via mechanical compressors, compared to hydrogen generated via high-pressure electrolysis, is much higher¹⁸.

There are several different technologies used for the compression of gases in the supply chain of P2X. Mechanical compression is widely used for industrial purposes, especially in AWE which operates at lower to ambient pressures. However, mechanical compression has several disadvantages, including the requirement of a lot of moving parts, hydrogen embrittlement and large energy consumption. Recent advances in our technological understanding of non-mechanical compression integrated with hydrogen electrolysis has proven to have several advantages over mechanical compression. Some advantages involve efficient isothermal compression and compact compression units with the absence of moving parts and high compactness¹³.

2.3.1 Mechanical Compression

Three technologies for mechanical compression (reciprocating compression, diaphragm compression and ionic liquid compression) were evaluated in this thesis.

Reciprocating Compressor

A reciprocating compressor uses positive displacements to compress and move volumes mechanically. The main mechanism of the device is the metal piston compressing the cylindrical compression chamber¹⁹.

Diaphragm Compressor

A diaphragm compressor is another type of mechanical compressor. In this compression unit, the hydrogen gas is completely isolated from the piston by a hydraulic fluid and a diaphragm membrane. The piston compresses the hydraulic fluid which in turn moves the membrane, hence compressing the gas. Diaphragm compressors are suitable for applications using lower flow rates. Operation at too high flow rates can lead to rupture and failure in the membrane. The compression unit is also limited to certain volumetric flows due to the volume of currently used compression chambers¹³.

Ionic Liquids Compressor

In an ionic liquid compressor, the metal piston in conventional compression is replaced with a nearly incompressible ionic liquid. The gas in the compression chamber is put under pressure of the up- and down movement of the ionic liquid pushed by a piston. The liquid and the gas are physically connected. However, they do not mix due to the nature of the liquid and hence, there is no need for seals and bearings in the compressor²⁰.

2.3.2 Non-mechanical Compression

Three technologies for non-mechanical compression (metal hydride, electrochemical compression, and adsorption-desorption compression) were evaluated in this thesis.

Metal Hydride Compressor

Metal hydride compressors have attracted significant interest recently due to their promising efficiencies. A metal hydride compressor operates thermally and uses the properties of different hydride-forming metals, alloys, or intermetallic materials in order to absorb and desorb hydrogen by controlling the heat transfer of the process. Hydrogen is absorbed at low temperatures and remains absorbed until the equilibrium pressure is equal to the feed pressure. Hydrogen is then desorbed when the metal hydrides are heated and released at higher pressures. Therefore, a multistage configuration is required in order to compress hydrogen up to pressures of 70 MPa, roughly 700 bar. The fundamental properties of the metal hydrides are of importance, and different types of compounds are necessary to be used in series, in order to

achieve an efficient compression. With higher operating temperatures of the first stage in the compressor and a descending temperature gradient across the series of metal hydrides resulting in a higher desorption pressure of the first stage compared to adsorption pressure of the next stage. The average operating temperatures of metal hydride compressors are typically around 573K^{13, 21}.

Electrochemical Compressor

Electrochemical compressors operate similarly to proton-exchange membrane fuel cells. Electrochemical cells consist of two electrodes, a polymer membrane and layers allowing gas diffusion. Low-pressure hydrogen is fed to the anode where the hydrogen is oxidised and spitted into protons and electrons under the application of electrical energy supplied to the system. Electrons are transported via the external electric circuit whilst protons are transported through the membrane to the cathode where the reduction reaction takes place. Here, hydrogen is recreated. Using backpressure regulators allows flow of hydrogen at a desired discharge pressure. The difference between an electrochemical cell and a proton-exchange membrane cell is the exclusion of oxygen, the cathode of an electrochemical cell is blocked and hence no air is introduced. Nafion®, a sulfonated tetrafluoroethylene based fluoropolymer-copolymer, is generally used as the type of membrane in this type of cell due to the high proton conductivity at low temperatures and the membrane-electrode assemblies (MEA*) consists of metal nanoparticles of platinum catalyst dispersed in in a solid electrolyte matrix precisely like in a PEM fuel cell¹³.

Adsorption-Desorption Compressor

An adsorption-desorption compressor operates very much like a metal hydride compressor. It is a thermally driven compressor where adsorption and desorption of hydrogen is coupled with thermal cycles of cooling and heating. Hydrogen is initially adsorbed at cryogenic temperatures of around 77 K, which is approximately the temperature of liquid nitrogen. It is generally accepted that the density of adsorbed hydrogen is approximated to the density of liquid hydrogen²², and the density of the adsorbed hydrogen increases the lower the temperature is. Under the typical cryogenic operating conditions, the density of the absorbed hydrogen is equal to 70.8 g/L. The compression of hydrogen originates from the desorption of hydrogen from the pre-absorbed amount. The hydrogen passes from a denser absorbed phase into a less dense bulk tank, a temperature driven process which is done by simply removing the cooling from liquid nitrogen. Alternately, cooling systems can be designed using microporous absorption material with high thermal conductivity for better kinetics¹³.

2.3.3 Evaluation

In general, non-mechanical compressors have several advantages over mechanical compressors. Most significant overall advantages are listed below:

- No moving components
- Quiet operation
- High reliability
- High safety

- Structural simplicity
- Greater compactness

Electrochemical hydrogen compression is a technology that offers high chemical stability and durability for above 60,000 h of operation¹³. The process is also purely chemical thus no moving parts are needed in the system. It has a proven high efficiency¹³ of 60% and the process provides an alternative isothermal compression which is more efficient than both adiabatic- and polytropic compression of hydrogen. However, the efficiency decreases with increased discharge pressure. Reducing the amount of high-pressure hydrogen at the outlet, a phenomenon known as “back-diffusion”. Therefore, this process alone is not suitable for high-pressure operations, but it is a very convenient technology for low-pressure operations due to its low cost, high hydrogen recovery and purity, low maintenance and finally low operating temperatures¹³.

Adsorption-desorption compression offers promising design possibilities. From an industrial point of view, the integration and access of liquid hydrogen at low temperatures are beneficial for the compression. Additionally, the use of activated carbon as an absorbent are currently studied and may prove to be an advantage in the future. However, the TRL as well as the flow rate capacity is too low for large-scale hydrogen production.

In terms of efficiency of hydrogen compression, the best mechanical compression is compression via ionic liquids. The device is capable of operating with high compression ratios using multiple steps and a specific energy consumption of 2.7 kWh/kg. In comparison, this value is almost 25% of the specific energy consumption of reciprocating compression. Moreover, these devices tend to have a very high efficiency for mechanical compression of around 70%¹³. However, these types of compressors are unable to handle large flow rates required for large-scale production of hydrogen, see Table 1.

Reciprocating compression has several disadvantages including the performance and the safety of the systems used. There are problems with the isolation of gas which are influenced by the moving components within the compressors. This allows leakage of gas from the compressor which in turn affects the overall efficiency of the compressor as well as the safety of operators risking hydrogen contamination and exposure of other hazardous chemicals. In the specific case of hydrogen compression, the metal parts of the compressor are experiencing hydrogen embrittlement to a larger degree, resulting in decreased mechanical performance and increased maintenance. Moving metal parts results in other types of maintenance involving lubricants and oils for parts that experiences greater friction in the process as well, like gears and valves. Another drawback with reciprocating compressors is the structural complexity of the unit involving many moving parts. Reciprocating compression is not suitable for large-scale compression due to the larger compression ratios resulting in a too large need of cylindrical compression chambers, which in turn results in difficulties in controlling the heat transfer and the cooling of compression. Finally, operators of these kind of compressors are exposed to loud operation noise in their working environment, which is a health risk worth mentioning, due to the structure of the reciprocating compressors¹³. An advantage of many different moving parts is the low-cost of repairs needed. Removing a defect part or repairing a part in a compressor is usually more cost efficient than replacing the whole compressor, which is the case for compact compression units.

Mechanical compressors are responsible for 54% of the CAPEX, 28% of total energy consumption and finally 18% OPEX of a hydrogen refuelling station¹³. For a direct Power-to-

hydrogen in a decentralised system, more efficient compression is necessary. By the same analogy, more efficient compression in e-methanol production is needed.

An advantage of diaphragm compression over reciprocating compression is the fact that the hydrogen is completely isolated from the metal piston which lowers risk of hydrogen embrittlement, lower gas leakage and the decrease of lubricants needed¹³. However, a drawback with this compression is the limited capacity due to the ratios of flow and mechanical stress on the membrane. This makes this compression unsuitable for large-scale compression of hydrogen.

The only viable option for large-scale e-methanol production, is the traditional mechanical reciprocating compression as it is the only technology with high enough flowrate capacity, see Table 1. Energy associated with the compression of hydrogen is responsible for a large portion of the operational costs delivering hydrogen up to the distributed pressure. Few technologies have a technical readiness level high enough for implementation and an interesting technology for high pressure electrolysis operation is the electrochemical compressor. However, further work and advancements in compression technology is needed to evaluate whether high pressure electrolysis reduces the energy cost²³.

Table 1: A summary of all technologies of compression evaluated in this thesis.³

Compressor Type	Max Flow [Nm ³ /h]	Max Pressure [MPa]	Method of Compression	Main Merit	Main Limitation
Reciprocating Compressor	4800	86	Positive displacement	Very high discharge pressure	Difficult Maintenance
Diaphragm Compressor	581	28	Positive displacement	Seal less design	Diaphragm failure
Ionic-Liquid Compressor	750	100	Positive displacement	Long lifetime	Cavitation phenomena
Metal-Hydride Compressor	10	30	Thermal	No moving parts	Low efficiency
Electrochemical Compressor	470	100	Electrochemical - Positive displacement	Low cost	Difficult manufacturing of MEA*
Adsorption-Desorption Compressor	560	10	Thermal	No moving parts	Thermal management difficulty

2.4 Transportation and Storage

There are several different methods for the distribution of produced hydrogen from the electrolysis. Methods commonly used are direct distribution via pipelines into other processes and this direct linkage in between processes is also the most energy efficient. Other means of distribution involves transport of highly pressurised hydrogen gas, liquefying the hydrogen at -253 °C, or conversion of hydrogen into hydrogen vectors such as ammonia and liquid organic hydrogen carriers (LOHCs): the former ammonia-based mean of transport is already used

extensively today whilst the latter is in an early stage of TRL, and further development is needed to make it commercially applicable. However, in each of these cases there is a significant energy loss due to the conversion. Around 0.5 – 11% of the total energy stored in hydrogen is lost due to compression and decompression and around 73% of the total energy is lost in conversion to ammonia and then back to hydrogen before end application. However, the reconversion cost from ammonia to hydrogen would not be incurred from an economical point of view²⁴.

The literature describes three different critical tipping points, taking volume of hydrogen and distance of transport into consideration, which defines the best available technology used for the distribution. The first tipping point applies to volumes above 10 tonnes per day and the recommended means of transport for these volumes are via pipelines. Pipelines are, in most cases, the most efficient option of transporting hydrogen. Lower-capacity pipelines transporting hydrogen levels below 100 tonnes a day are preferred for smaller local networks with a transport range of up to hundreds of kilometres. Large-capacity pipelines (transmission pipeline) are preferred for transporting hydrogen levels beyond 100 tonnes a day and will be the most economically favourable and with a range of up to 1000 kilometres of transporting distance²⁴.

Today there are only 4500 km of hydrogen pipelines operational worldwide with the longest being 500 km. In contrast, there is 3 million kilometres of natural gas pipelines. It is highly likely that there will be a significant increase in the pipeline-network for hydrogen in the near future. A possibility is retrofitting of existing high-capacity gas pipelines which would cost approximately 40 – 65% of new pipeline construction²⁴.

The second tipping point is for high-capacity intercontinental transport of more than 100 tonnes per day and at distances over thousands of kilometres. The shipping involves converting the hydrogen into liquid ammonia in order to fill carrying tanks with as much as possible. If ammonia is the end-product to be used, then short-distance shipping could also be economically favourable by avoiding high-cost reconversion and large deliveries²⁴.

The third tipping point is for the transportation of volumes below 10 tonnes a day and less than about 200 km. Here, the most cost-effective option is to liquefy the hydrogen and transport the hydrogen via trucks²⁴.

2.5 Carbon Capture

Increasing levels of carbon dioxide emissions are intensifying the effects of pollution on our environment. Industrial carbon emissions, apart from power plant, stand for around a quarter of the global emissions and the three main sectors that contribute to 70% of the industrial carbon emissions are: Iron and steel (a third), the cement sector (27%) and finally the oil refining, petrol production and transformation of fuels (10%)²⁵. Technologies for carbon capture and storage (CCS) are in advancement and provide means of operation that significantly reduce the carbon emissions from industrial processes. These technologies involve the capture of carbon dioxide prior to the emission from larger industrial facilities and production sites for processing and storage underground in specifically design reservoirs and vessels. This approach is widely accepted as future solution to the increasing global emissions. However, the recirculation of purified carbon dioxide into other industrial processes are potentially a more attractive alternative, referring to the utilisation of captured carbon dioxide also known as CCSU. This utilisation of captured carbon dioxide provides the raw materials used for the production of e-methanol.

Capturing carbon dioxide requires significant amounts of energy and, in terms of energy efficiency, the penalty for capture is often measured in a fractional reduction of energy input and energy output of the plant. The efficiency of the carbon capture plant is very dependent on the technology implemented and efficiencies varies between the three main process-models (post-combustion, pre-combustion, and oxy-combustion)²⁵.

In post-combustion capture, the carbon dioxide is captured from flue gases, just before the flue gas is supposed to be emitted, that contain relatively low volumetric percentages of carbon dioxide (around 5 – 15%). Most of the flue gases contain nitrogen and oxygen as well as some amounts of NO_x and SO_x. The most prevalent technologies involving commercialised carbon capture, that still undergoes a lot of development to increase efficiency, involves absorption in solvents and subsequently solvent regeneration, often in combination with membrane separation. However, amine-based carbon capture has been commercialised for decades. Newly developed technologies involving chilled ammonia is implemented widely, especially in Europe and North America, in smaller plant sizes and oil refineries^{25, 26}.

Pre-combustion is mostly implemented at coal and natural-gas plants. Here, the carbon is extracted from the fuel before combustion. The fuel reacts with air or oxygen and is further processed in a shift reactor to produce a mixture of hydrogen and carbon dioxide. Carbon dioxide is capture from a high-pressure stream containing between 15 – 40% carbon dioxide^{25, 26}.

Oxy-combustion process involves the removal of nitrogen from air streams. This is a very new technology and technical advances allow usage of an air separation unit or membranes in combination with chemical looping cycles which is considered promising for the future of carbon capture. As a result of the nitrogen separation, the nearly pure oxygen stream is combusted with the fossil fuel in recycled flue gas in order to control the temperature of the combustion. This results in a flue gas of mostly carbon dioxide and water vapour^{25, 26}.

Post-combustion is the most developed technology, and in terms of technology development with respect to combustion type, it is the most mature of the combustion types with 76% of the literature supporting technologies in carbon capture falling under this category²⁷.

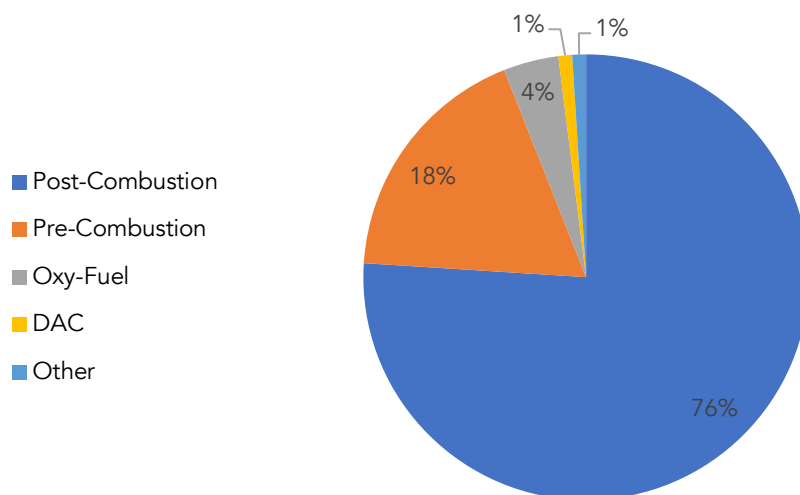


Figure 8: Shows the distribution of technologies claiming to be innovative in carbon capture processes, identified by FutureBridge. The figure shows that post-combustion is predominantly the most developed of these combustion technologies for carbon capture. Inspiration taken from Concaawe.eu. https://www.concaawe.eu/wp-content/uploads/Rpt_20-18.pdf (accessed 2023-05-09).

Traditional post-combustion carbon capture technologies, using solvents, involve an absorber and a desorber used for chemical absorption and desorption. It also includes membrane separation units and chemical looping combustion processes, as well as underground storage and distribution systems of high purity carbon dioxide. Other technologies involve the use of sorbents on solids in order to absorb the carbon dioxide²⁷. Usually, the flue gas is transported, cleaned, and cooled before entering the bottom of the absorber where the flue gas encounters the absorbent entering the top of the absorber. The flue gas that leaves the absorber at the top, has a low-carbon content, and is emitted to the atmosphere. The carbon-rich absorbent in the bottom of the absorber is transported to the desorber and heated to release its carbon content. Most of the carbon capture technologies utilise the regeneration of absorbents. Thus, after the release of the carbon, the absorbent is then regenerated and transported back to the absorber for re-use^{25, 28}.

2.5.1 Amines

This technology revolves around the use of amine-based absorbents for post-combustion capture. Monoethanolamine (MEA) is the most conventionally used absorbent in the industry today. The reaction taking place between the amine and the carbon dioxide can be a zwitterion mechanism²⁹. The reaction can be described by the intermediate formation of a zwitterion when the amine reacts with the carbon dioxide. If the amine is unhindered, the amine itself deprotonates the zwitterion allowing the formation of a stable carbamate ion. This indicates that the maximum amount of carbon dioxide that can be reacted with an unhindered amine is 0.5 mol per mole amine²⁹. See Reaction 9 for the overall reaction via an unhindered amine.



Another amine used in post-combustion capture is KS-1, a sterically hindered amine developed by the Mitsubishi Heavy Industries and Kansai Electric Power Company³⁰. A sterically

hindered amine is defined either as primary amine in which the amino group of the molecule is attached to a tertiary carbon or as a secondary amine where the amino group is attached to at least a secondary or tertiary carbon. The reaction between a sterically hindered amine and carbon dioxide is different in comparison to Reaction 9. The hindrance of the alkyl group inhibits the formation of stable carbamate ion and hydrolysis to a bicarbonate ion is favoured instead. The maximum amount of carbon dioxide that can be reacted with an hindered amine is 1 mol per mole amine²⁹. See Reaction 10 for the overall reaction via a hindered amine.



KS-1 is showing great potential compared to the conventional MEA-based absorbent due to the molar ratio of the primary reaction of 1:1 amine: carbon dioxide²⁶, less heat requirement and reduced solvent degradation³⁰. Another post-combustion technology is the chilled ammonia process (CAP) which is a process that addresses the challenge of removing carbon dioxide at ambient pressures and lower temperatures. The process uses ammoniated aqueous carbonate solution to absorb carbon dioxide from the flue gas entering the absorber.

The three amine-based absorbents mentioned (MEA, KS-1 and CAP) are the most commonly used for post-combustion carbon capture with the use of KS-1 still under development. Reactions involving amines often uses catalyst, such as piperazine, to increase the reaction kinetics²⁷.

2.5.2 Alkaline

This technology uses aqueous alkaline solutions impregnated on solid surfaces and used as absorbents for the absorption of carbon dioxide in packed towers. The use alkaline solutions, such as NaOH and KOH, produces hydroxides which interacts strongly with carbon dioxide, hence a high absorption efficiency³¹.

2.5.4 Evaluation

The KS-1 absorbent shows many advantages over the conventional MEA-based absorbent primary since the absorbent requires less molar quantity to recover carbon dioxide from the flue gas stream³². It also requires less regeneration energy due to the stable carbonate product formed during the MEA-based reaction³². Other advantages of KS-1 are that it has a higher carbon dioxide loading per mole of amine under ambient temperatures and because its less corrosive nature, lowering the amount of corrosion inhibitors required³². KS-1 alone, can also reduce the steam consumption with 20% compared to MEA and it is also able to produce high purity carbon dioxide streams of >99,9% carbon content which can be directly distributed for industrial use in e-methanol production and other general purposes³³. KS-1 has proven to have a very high technical readiness level and could therefore, be a better alternative than MEA.

Organic amines used as solvent, including MEA and KS-1, shows tendency to degrade when exposed to high temperatures (thermal degradation), exposed to oxygen (oxidative degradation) and in acid gas reactions (such as NO_x)³⁴. This degradation results in reduced performance of the absorption, loss of solvent, higher risk of corrosion on equipment and the potential formation of cancerogenic volatile components, including nitrosamine, emitted into the flue gas leaving the plant³⁴. These risk-factors associated with the degradation of solvent is absent from the CAP due to the inorganic amine-based solvent used in the process. Another advantage with

CAP is that it allows regeneration of carbon dioxide at elevated pressures which in turn reduces energy cost for the pressurisation of carbon dioxide downstream³⁵. A design capacity of 100 ktpa of carbon dioxide for CAP has been validated at several test facilities, one being located in Norway with a capacity of 80 ktpa of carbon dioxide and has been in operation for the past years, showing great potential³⁵. Furthermore, ammonia is a low-cost commodity chemical widely used and available on the global market from many suppliers. It is also stable, tolerant to flue gas contaminants, such as NO_x and SO_x and typically exhibits low and controllable absorbent losses during process operations in CAP. A prominent advantage with the use of ammonia as absorbent is that it can be produced from green hydrogen, hence, suited for industrial transition to renewable usage of resources. One drawback with chilled ammonia as solvent, in comparison to organic amines, is the lower technical readiness level³⁵.

Alkaline solutions used as absorbents has been prized for their high efficiency in terms of absorption. However, the use of alkaline solutions, such as NaOH and KOH, increases the risk of corrosion and these solutions are not regeneratable resulting in increased operational- and maintenance costs. For these reasons the development of alkaline solutions has decelerated and technologies involving recycle resources has been considered more prominent²⁸.

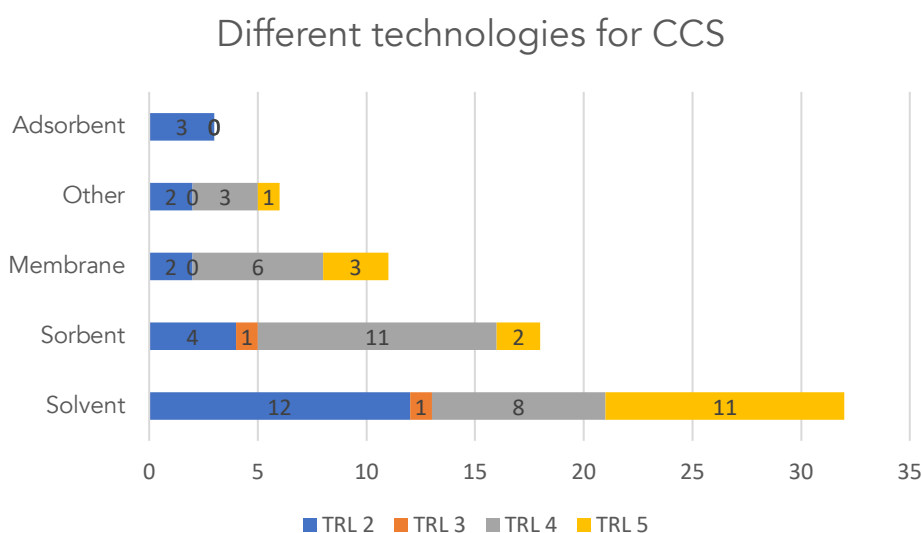


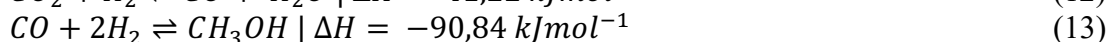
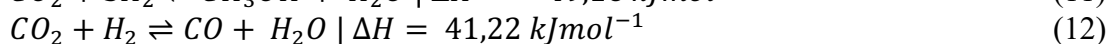
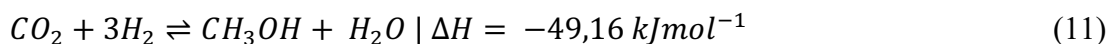
Figure 9: FutureBridge has identified technologies using solvents as the predominantly most mature technologies on the market today. Inspiration taken from Concaawe.eu. https://www.concaawe.eu/wp-content/uploads/Rpt_20-18.pdf (accessed 2023-05-09).

Even if pre-combustion is more efficient in comparison to post-combustion, the pre-combustion is about two times more expensive in terms of capital investment associated with the system³⁶. Furthermore, there are a limited amounts of implementations of pre-combustion carbon capture and these technologies are still under development. To achieve feasible results, better integrations of syngas systems are developing. Hence, these technologies are too immature and therefore not suitable for large scale operation. Oxy-combustion technologies are still under development and have a low technology readiness level, therefore they are not considered in this project. The undoubtedly most preferred and most commonly used solvent for large-scale commercialisation is MEA²⁷. Therefore, it is also considered as solvent for the CCUS-plant in this project.

2.6 E-Methanol Synthesis

E-methanol is the end product in the P2X process chain covered in this thesis. The most commercialised way of large-scale production of methanol includes the production via natural gas or coal sources³⁷. Natural gas is conventionally processed into, a mixture of hydrogen, carbon monoxide and carbon dioxide. Therefore, the production pathway of conventional syngas is not in line with the scope of this thesis. However, there are emerging technologies that can produce fossil-free syngas (biosyngas) but these technologies have a low TRL, according to a survey answered by 32 experts in the field. In summary, the asked experts expressed lack of long-term experience with large-scale units, uncertain economic boundaries, high investment costs, negative experience and -general public perception of bio gasification³⁸. Therefore, e-methanol production via biosyngas and the production pathway using conventional syngas was not considered in this thesis.

With the use of pure reactant sources, the chemistry behind the production of e-methanol can be simplified into CO₂-hydrogenation, see Reaction 11, and reverse water gas shift (RWGS), see Reaction 12, whilst the CO-hydrogenation can be simplified to Reaction 13³⁹:



It can be noted that the main CO₂-hydrogenation is exothermic whilst the reverse water gas shift reaction is endothermic and undesired, producing carbon monoxide⁴⁰. Therefore, the main concern in methanol synthesis remains as the removal of excess heat generated by the reaction. Traditional ways of dealing with this include external coolant systems or stage conversion systems with intermediate cooling in between stages often in the form of quenching or cold-shots of gas injections³⁹.

The extraction of crude methanol often involves extensive and separate purifications steps in order to remove multiple gas impurities and liquid coproducts. In methanol synthesis from pure sources, it is common to take advantage of the reduced amounts of by-product formed, such as methane, ketones, heavy alcohols etc., compared to conventional use of CO-hydrogenation. This is beneficial and enables purification via light-end separation processes instead. The light-end process is necessary because of the high solubility of carbon dioxide in methanol and separation via flash operations are simply not adequate³⁹.

2.6.1 Reactor

Typically, carbon dioxide hydrogenation is carried out in a adiabatic fixed bed catalytic reactor at 250-300 °C at 50 bar is currently the operational process with the largest development at an industrialised large scale⁵. Other reactor types used in CO₂-hydrogenation is quasi-isothermal reactors.

Quasi-isothermal reactors are usually water-cooled tubular reactors where the reaction takes place inside the tubes, and the cooling of water is shell sided⁴¹. However, quasi-isothermal reactor designs have several advantages over adiabatic ones. The quasi-isothermal reactor design allows for better temperature control and lower average reaction temperatures in the

catalytic bed, in turn decreasing the amount of by-products formed (Reaction 13) and decreased catalyst degradation. Therefore, quasi-isothermal reactors have a higher efficiency, expressed in space time yield, in comparison to adiabatic ones⁴¹.

2.6.2 Catalyst

The most commonly used catalyst for methanol synthesis is a Cu/Zn/Al based catalyst, mainly due to its high selectivity, stability and activity⁴². Both carbon dioxide-based and carbon monoxide-based methanol synthesis involve the same three reversible reactions (11-13). Therefore, it is possible to apply the same catalyst for synthesis from both carbon sources. However, specially designed catalyst designated for the synthesis from carbon dioxide feedstock results in the highest productivities⁴¹.

A lot of research and efforts into optimising the conversion rate of methanol production has paved way for advanced catalyst design⁵. The main problem with the optimisation of catalyst usage has been the correlation of production demand and minimisation of cost. It was concluded by Saad, D. M., et al. that lower production rates of 5000 kg/h favoured alternative routes of methanol production via dimethyl ether (DME), using Cu-Zn-Al-La/HZSM-5 catalyst was most promising. However, increasing production demand reduced the cost-efficiency and the model suggested that if production demand increased to 25,000 kg/h, the use of other copper/zinc-based catalysts for direct methanol production was the most favorable pathways in 61% of the cases studied⁴³. These catalysts also contain other elements such as Al, Zr, Cr, Si, B, Ga for improved catalytic performance⁵.

2.6.3 Evaluation

The productivity measured in space-time yield was reportedly higher for carbon-monoxide-based synthesis in a test plant and simulation conducted by Lurgi, reported by Pontzen et al⁴⁴. However, the carbon dioxide-based synthesis is more selective producing up to five times less by-products, excluding water, in comparison. The main contributing factor to the lower production of by-products is due to the lower temperatures in the catalytic bed⁴⁴.

The use of copper-zinc based catalysts are the most optimal choice for large-scale production of methanol. Copper being the catalytic species whilst elements like Al reduces the catalytic sintering. The copper-zinc based catalyst also reduces the operating pressures to between 5 MPa to 10 MPa which result in large cost savings in terms of lower operational cost. In addition, improving the chemical equilibrium reduces operational temperatures to between 200 – 250 °C, further decreasing operational costs⁴⁵.

Conventional reactor configurations used for the crucial temperature control of operation often involving the adiabatic or cold-shot reactor. However, these configurations have proven to have lower efficiency and higher operational costs in comparison to tube-cooled quasi-isothermal reactors^{41, 46}. Additionally, the tube-cooled reactor also provides simplified operation due to the adiabatic and cold-shot reactors may require multiple reactors in series to achieve a desired conversion³⁹. Further, improvements of heat control of the reactor prevents catalyst sintering hence reducing process interruptions and catalyst costs³⁹. Therefore, a tubular isothermal type of reactor was considered for this project simulation of the methanol synthesis loop in Aspen Plus.

2.7 Risk and Safety Management

Most of the risks and safety- issues related to e-methanol production are associated with hydrogen production and handling. Hydrogen is the smallest molecule in our universe which makes it prone to leakage. The primary hazards associated with handling gaseous or liquid hydrogen are explosion, asphyxiation, and exposure to extremely low temperatures⁴⁷.

Hydrogen gas has significantly lower density in comparison to air, under normal pressures and temperatures. Hence making the gas rise and potentially accumulate in the top of the ceiling, in closed compartments, making the density close to the ceiling much higher. However, this is potentially beneficial in open spaces like outdoors since hydrogen accumulation in concentrated areas would not occur. The risk with high concentrations of accumulated hydrogen is that the gas is highly flammable between concentrations in mixtures of air with 4 – 75 v/v% hydrogen⁴⁷ and in mixtures of oxygen within 4 – 94 v/v% hydrogen⁴⁸. Additionally, the ignition energies for these flammable hydrogen-air or hydrogen-oxygen mixtures are very low (0.02 millijoules for hydrogen-air mixtures which is less than 7% of the energy needed to ignite natural gas⁴⁸) and can ignite from spark, heat, or sunlight⁴⁷. Therefore, keeping hydrogen from mixing with air or oxygen in confined spaces is crucial for safety management.

Hydrogen reacts with every oxidising element and especially it reacts spontaneously and violently with chlorine and fluorine, under room temperature, to form halides which are potentially hazardous acids if exposed to⁴⁷.

Additionally, hydrogen needs to be contained using specialised materials and designs in order to account for hydrogen embrittlement which can cause materials to fail especially under high pressures. Therefore, compressors with a lot of moving parts consequently leading to a higher likelihood of hydrogen leakage, have extensive sealing systems and are made of elements less susceptible to embrittlement such as steel, copper, aluminium, and brass in order to allow safe operation⁴⁷.

Other safety risk with mechanical compressors is the exposure to loud noise during operation which needs to be taken into safety-consideration for workers. Generally, when operating under high pressures and temperatures, compared to normal circumstances, more safety precautions are needed.

3 Basis of Design

This section covers the production chain of e-methanol and all major units involved, in large-scale production of 46,000 ton e-methanol/year which is around half the capacity of the world's current largest e-methanol plant (110,000 ton e-methanol/year, in Anyang, Henan Province, China). Furthermore, this size is deemed reasonable for potential future e-methanol projects in accordance with AFRY. In this section the process is described with basis in assumptions made in Section 3.4 and design specifications (such as design capacity and design parameters) are presented in text and in Tables 2-7.

3.1 Process Description

A very basic and schematic process flow diagram can be seen in Figure 10, that highlights the major processes in the production chain in e-methanol via direct CO₂-hydrogenation. The schematic figure illustrates buffer tanks that allows continuity in production of e-methanol, with regards to the intermittent nature of renewable resources. Carbon dioxide is compressed to 20 bar and stored in liquid phase whilst both hydrogen and oxygen is compressed to 200 bar and stored in a buffer tank and bottled tubes respectively.

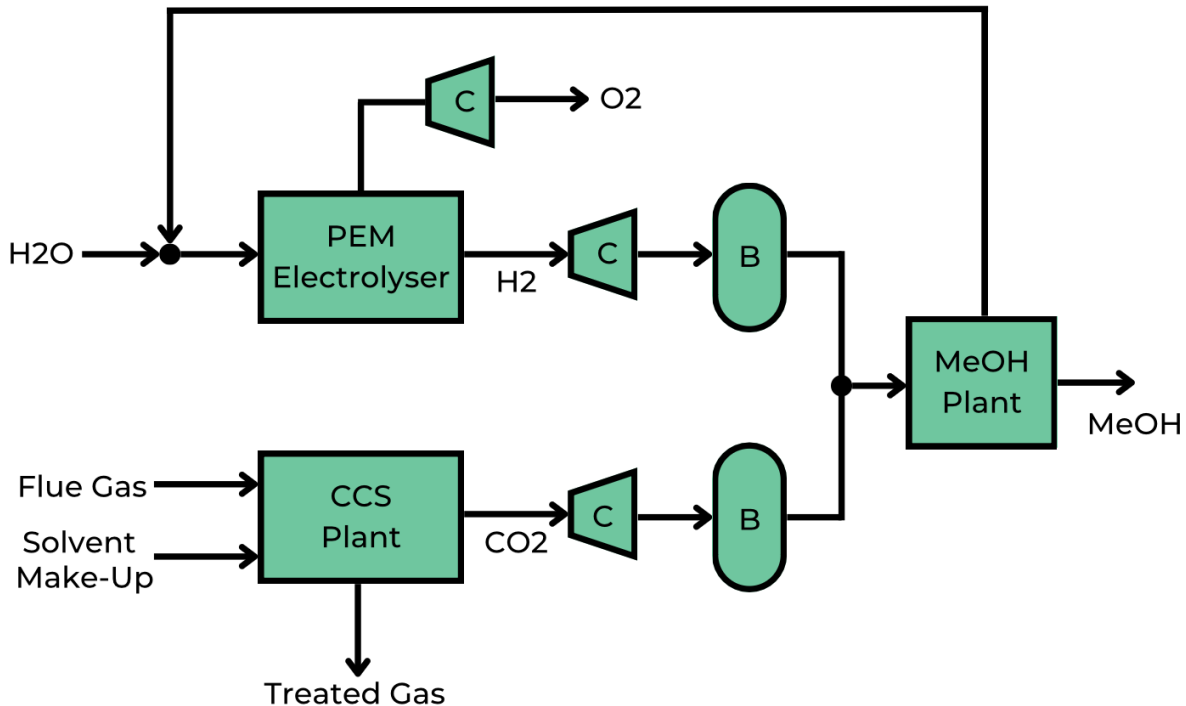


Figure 10: Shows an overall simplified view of the e-methanol process via direct CO₂-hydrogenation, highlighting the major units involved in the process chain. C = compressors and B = buffer tanks.

3.2 Design Capacity

The e-methanol production capacity is 46,000 tonnes/year, the plant is estimated to be operational 333 days a year with continuous operation, equivalent to 8000 h of operation a year.

The PEM electrolyser needs to have a power capacity of 67 MW, considering the specific power consumption⁴⁹ of 55,5 kWh/kg of produced H₂ and with a total inlet flow of hydrogen to the methanol synthesis system of 1204 kg/h.

The CCS plant is expected to have a removal efficiency of carbon dioxide of 90% and be capable of producing a CO₂ stream of at least 8000 kg/h into the methanol synthesis loop. Hence an exhaust inlet of treated flue gases of around 49,000 kg/h with a concentration of CO₂ of around 18%.

3.3 Design Parameters

This section consists of Tables 2-7, showing the parameters used in Aspen Plus V.11 simulation and cost estimate, in Section 6.

Table 2: The different operational units used in Aspen Plus V.11 for the simulation of the methanol system with a capacity to produce 46,000 ton/year.

Reactor	RPlug
Distillation column	RadFrac
Liquid-Vapor Separators	Flash2
Separator	Sep
Multi-stage Compressors	MCompr

Table 3: Summary of parameters used for the simulation of the methanol system in Aspen Plus V.11 and values used for cost estimations for an e-methanol plant with a capacity to produce 46,000 ton/year.

Flow rate of methanol from system	5750 kg/h
Flow rate of hydrogen into system	1204 kg/h
Flow rate of carbon dioxide into system	8000 kg/h
Annual production of methanol	46 000 tonnes
Recirculation flow rate	15 997 kg/h
Outlet carbon dioxide flow rate	30.7 kg/h
Amount of catalyst into reactor	122 348 kg
Number of tubes	4450
Inner diameter of each tube	0.0375 m
Length of each tube	12.2 m
Residence Time	0.44 min
Reactor volume	61.17 m ³
Type of catalyst	Cu/Zn/Al
Bed voidage	0.5
Catalyst density	2000 kg/m ³
Catalyst lifetime	4 years
Catalyst cost	95.24 €/kg
Operating pressure	65 bar
Inlet temperature to reactor	210 °C
Outlet temperature from reactor	250 °C

Table 4: Parameters for the separation units used in the simulation of the methanol system in Aspen Plus V.11.

Type of separation	Liquid-vapor
Operating conditions: first separator	50 °C, 65 bar
Operating conditions: second separator	22 °C, 1.2 bar
Composition out of second separator	48.7 %v MeOH: 49.4 %v H ₂ O
Temperature in distillation column	80 °C
Pressure in distillation column	1.01 bar
Composition of distillate out of column	96.4%v MeOH: 3.9%v CO ₂

Table 5: Parameters used to simulate the multi-stage compressors in Aspen Plus V.11.

Multi-stage Compressor (COMP1)	Number of Stages: 3
Multi-stage Compressor (COMP2)	Number of Stages: 2
Multi-stage Compressor (COMP3)	Number of Stages: 6
Isentropic Efficiency	72%
Pressure Ratio (Between stages)	Equal

Table 6: Parameters used for the estimation of the CCS-plant with a capacity to provide the methanol system with a flow of 8000 kg/h of captured CO₂. The values of MEA consumption and electrical energy cost are presented by X. Zhang, et. al.⁵⁰ and the specific cost of MEA was adopted from S. Sollai, et. al.⁵.

Absorbent	Amines (MEA)
CO ₂ Concentration in Flue Gas	18%
Pressure of Outlet CO ₂	2 bar
Exhaust inlet	49 ton/h
CO ₂ Removal Efficiency	90%
Carbon Captured	8000 kg/h
Annual Carbon Capture	64 000 tonnes
MEA Loading	30%
MEA Consumption	1.5 kg/ton CO ₂
MEA Specific Cost	1.9 €/kg
Electrical Energy Cost	1.348 MJ _e /kg CO ₂
Electricity Price	57.8 €/MWh

Table 7: Parameters for the PEM electrolyser with a capacity to provide the methanol system with 1204 kg/h.

Type	PEM
Capacity	67 MW
Flow Rate of Produced Hydrogen	1204 kg/h
Annual Production Hydrogen	9632 tonnes
Flow Rate of Produced Oxygen	9632 kg/h
Annual Production of Oxygen	77 056 tonnes
Pressure	30 bar
Operating Temperature	80 °C
Power Consumption	55.5 kWh/ kg H ₂

3.4 Assumptions

- To enable methanol synthesis from renewable resources (e-methanol) storage tanks was adopted, operating at 200 bar for temporary storage of hydrogen during low energy flux to enable buffer systems for continuous supply to the methanol synthesis process. A storage tank, operating at 20 bar, -24 °C was assumed for liquified carbon dioxide storage.
- The reactor was assumed to operate at a fixed temperature, assuming a quasi-isothermal tubular reactor is operated. However, in industrial applications the reactor needs to be thermally controlled via reactor design and heat exchanger fluids ensuring a stable

temperature profile throughout the whole reactor. This heat configuration system was not simulated.

- The excess heat from the reactor would beneficially be extracted to help drive other heat utilities such as reboilers in separation units. However, this simulated but only discussed.
- The mol purity and the pressure of the produced e-methanol is assumed to be 99.9% and 1.1 bar⁵¹.
- The distribution and storage of produced methanol is not taken into consideration in this project. The cost estimates are calculated based on the pure methanol stream, according to specified purity, that leaves the synthesis loop.
- For Aspen Simulation, continuous power supply was assumed.
- Access of cold water for heating- and cooling systems, as well as. Other necessary utilities were assumed and not considered for the cost estimation of the e-methanol plant.
- The price of industrial electricity was assumed to 57.8 €/MWh, as well as 30 €/MWH based on futuristic scenarios of decreased inflation, advancements in energy technology and overproduction of electricity.
- Given diameters and lengths of tubes in reactor was assumed⁵². These measurements are not optimised in the simulation.
- No effect of CO-hydrogenation in the methanol synthesis was assumed.
- Neglectable maintenance and operational costs for buffer tanks and compression was assumed. These tanks are located at the methanol plant hence operated by the employees of the plant.
- Flue gas was cleaned from NO_x, SO_x etc., pressurised and distributed by the power plant to the CCS-plant.

4. Process Simulation

The methanol synthesis process was simulated in Aspen Plus V.11 using validated kinetics and models highlighted in the literature, see Figure 11 for process flowsheet. The system was later optimised, in attempts to increase efficiencies, after reaching convergence of simulated synthesis loop.

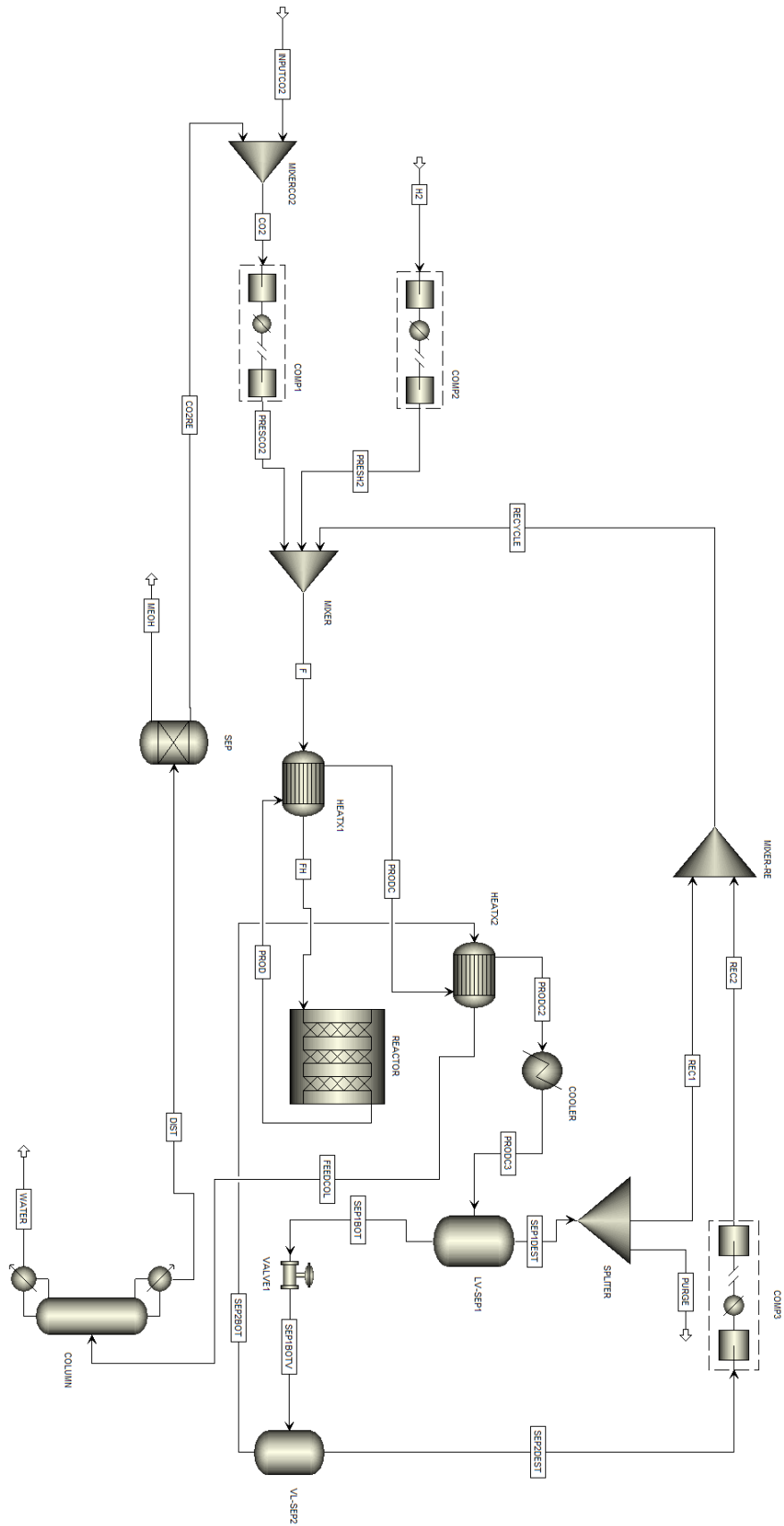


Figure 11: The flowsheet of the methanol system simulated in Aspen Plus V.11 with a capacity to produce 46,000 ton/year.

Hydrogen and carbon dioxide streams are compressed to 65 bar, which is the operating pressure of the methanol reactor, in multi-stage compressors with equal pressure ratio between stages. The streams are mixed with a recirculation stream and pre-heated with the product stream leaving the reactor, to increase the conversion efficiency. The reactor is operated under conditions typically used in industrial processes: The inlet temperature to the reactor is set at 210 °C, and the heat of reaction elevates the operating temperature in the reactor to 250 °C. The heat transfer fluid (boiling stream) removes the excess heat from the reactor for temperature control to enhance conversion per pass and prolong lifetime of catalyst. The product stream leaving the reactor is later cooled and the unconverted gas is separated from the liquid phase through two flash vessels. The unconverted gas, recirculated to the reactor, mainly consist of hydrogen and carbon dioxide with small traces of methanol, water and carbon monoxide. The stream leaving the top of the second flash vessel is compressed in a multi-stage compressor with equal pressure ratio in all stages. About 1% is purged and flared in order to prevent accumulation of inert gas and undesired gas in the circuit. This contributes to small amounts of CO₂ emissions, around 30 kg/h, which is neglectable considering that this contributes to almost 0.4 % of the carbon captured from the flue gas leaving the system⁵.

The raw methanol exiting at the bottom of the second flash vessel contains small traces of water and CO₂. This stream of raw methanol is heated to the operating temperature of the distillation column before entering the column. The flashed vapor exiting the top of the second flash vessel is cooled and compressed to the operating pressure of the reactor in a multistage compressor with intermediate cooling. Water is compensated and collected at the bottom of the distillation column whilst the distillate consists of methanol and CO₂. The process is theoretically thermally self-sufficient during operation due to the heat transfer optimisation of multiple operating heat exchangers⁵.

4.1 Reactor Kinetics

The maximised conversion rate was supposed to be achieved when the stoichiometric molar ratio $M = 2$, see Equation 1⁵¹.

$$M = \frac{[H_2]-[CO_2]}{[CO]+[CO_2]} \quad (\text{Equation 1})$$

The reaction kinetic models used in the reactor model were derived over a Cu/ZnO/Al₂O₃ catalyst and was selected due to their simplicity⁵¹ and the widely common use as kinetic models in methanol synthesis⁵³. The kinetic model was based on a Langmuir-Hinshelwood/Hougen-Watson (LHHW) mechanism. The rate expression of the LHHW is based on a kinetic factor and driving force factor in the nominator, and an adsorption term in the denominator, see Equation 2.

$$r = \frac{(\text{kinetic factor}) * (\text{driving force factor})}{(\text{adsorption term})^n} \quad (\text{Equation 2})$$

The kinetic factor contains coefficients that govern the catalytic activity, surface reaction rate and the number of active catalytic sites whilst the driving force factor is based on the identified rate controlling reaction in the system. The adsorption term describes the number of available

catalytic sites and is put to the power of n, which represents the number of catalytic involved in the molecular reaction⁵³.

The pre-exponential values, activation energies and equilibrium constants, that these factors and terms of Equation 2 contains, are presented in work of K. M. V. Bussche et. al.⁵⁴. The kinetic models assume one catalytic site for the reacting species and include competition between CO₂ and CO for the active catalytic sites. However, models assuming different active sites for the species can also be applicable⁵¹. Kinetic models were chosen instead of an equilibrium conversion approach since the kinetic models ensures that equilibrium conversion is not reached and thus, gives a more accurate estimation of sizing affecting the capital- and operational costs⁵¹. The following kinetic models were used, neglecting the effect of the CO-hydrogenation reaction:

$$r_{MeOH} = \frac{k_1 P_{CO_2} P_{H_2} - k_6 P_{H_2O} P_{MeOH} P_{H_2}^{-2}}{(1 + K_2 P_{H_2O} P_{H_2}^{-1} + K_3 P_{H_2}^{0.5} + K_4 P_{H_2O})^3} \left[\frac{kmol}{sec * kg_{cat}} \right] \quad (\text{Equation 3})$$

$$r_{RWGS} = \frac{k_5 P_{CO_2} - k_7 P_{H_2O} P_{CO} P_{H_2}^{-1}}{1 + K_2 P_{H_2O} P_{H_2}^{-1} + K_3 P_{H_2}^{0.5} + K_4 P_{H_2O}} \left[\frac{kmol}{sec * kg_{cat}} \right] \quad (\text{Equation 4})$$

The equilibrium constants, pre-exponential factors and activation energies are expressed according to the work of Van den Bussche and Froment⁵⁴, and are converted into Arrhenius terms recognised by Aspen Plus, see Table 8.

Table 8: Kinetic parameters, expressed in Arrhenius terms, used in the Aspen Plus V.11 modelling of the RPlug reactor.

Parameter	A _i	B _i	Unit
<i>k</i> ₁	-29,87	4811.2	Pa ⁻²
<i>K</i> ₂	8,147	0	-
<i>K</i> ₃	-6,452	2068.4	Pa ^{-0.5}
<i>K</i> ₄	-34,95	14928.9	Pa ⁻¹
<i>k</i> ₅	4,804	-11797.5	Pa ⁻¹
<i>k</i> ₆	17,55	-2249.8	-
<i>k</i> ₇	0,131	-7023.5	Pa ⁻¹

Methanol synthesis operates under pressures greater than 10 bar. Therefore, a physical property method predicting equation of state is recommended by the “Property Method Selection Assistant”. Such models include “SR-POLAR”, “SRK”, and “PSRK”⁵². The chosen method was “SRK”.

4.2 Simulation Results

The single pass conversion of CO₂ of the reaction was 65%. However, with the recycle streams the overall conversion rate of CO₂ reached over 99.5%. The yield of methanol was 65,4% based on the limited reactant, in this case CO₂. The selectivity of the formation of methanol in relation to CO₂ was 99.7%, excluding water. Equations A1-A3 was used to calculate the results of the methanol synthesis loop, see Appendix A.

4.3 Simulation Discussion

In order to maximise conversion rates in the reactor by keeping a favourable stoichiometric ratio of the feed, as well as avoiding accumulation of unreacted species in the system loop, a design specification in Aspen (representing a PID-controller) was added that took into account the amount of each recirculated species and regulated the input mass flows of both hydrogen and carbon dioxide. The stoichiometric ratio of hydrogen/carbon dioxide, in the reactor inlet, that proved to generate the highest conversion rate of carbon dioxide, when tested, was a 22/1 molar ratio suggested in a study by Viet Hung Nguyen⁵⁵, without catalyst degradation.

A design spec regulated the minimum number of tubes needed in the reactor to keep a high conversion rate. The total number of tubes were decreased from 8000 to 4540, originally set by default in literature⁵² for the CO₂-hydrogenation. Due to many sources using much fewer tubes in CO₂-hydrogenation reactors, the capital cost estimation was based on a general purchase equipment cost (PEC) equation instead. The generated value from Equation 6, was also validated in comparison to the generated PEC value from the simulation in Aspen Plus.

There are several studies suggesting contradicting results whether CO-hydrogenation could be neglectable or not. The kinetic models used in this study originates from the work of Van den Bussche and Froment⁵⁴ which neglects the CO-hydrogenation. This was also strengthened by the work of Mbatha, S. et. al.⁵⁶ who proved that there are errors in some kinetic model using CO-hydrogenation^{57, 58}. This led to the exclusion of kinetic models taking CO-hydrogenation into account in this thesis.

In practice there would be formation of some traces of undesired products that has not fully been evaluated in the simulated methanol synthesis. CO₂-hydrogenation forms significantly less and potentially neglectable amounts of by-products in comparison to traditional methanol synthesis and none of the literature, that was studied in this thesis, presented any kinetics involving the formation of by-products such as methane, ketones, heavy alcohols etc. If the formation of these by-products are present in the reactor, the flowsheet in Aspen Plus needs to be re-modelled in order to take new kinetics and further separation into account.

Furthermore, formation of intermediates during CO₂-hydrogenation could be analysed as well for better quantitative results of the simulation. Especially since some of the intermediates, like graphitic carbon, decreases the catalytic activity⁵⁹. Additionally, since the kinetic models used for the simulation in this project only accounts for the CO₂-hydrogenation and the reverse water gas shift reaction, the accumulation of CO in the system is only handled via the purge stream. It remains uncertain to which extent the CO-hydrogenation contributes to the overall yield of methanol and different sources contradict each other^{60, 61}. Alternatively, the involvement of more advanced reaction kinetics can be taken into consideration in future works or the addition of streams containing intermediates can be inserted into the simulation system to analyse the effects and resemble more realistic methanol synthesis.

More extensive optimisations of the methanol synthesis loop could be done. These optimisations include pinch analysis in order to determine which areas of the process where heat can be utilised. Other means of optimisations could involve the configuration of operating units in the system. These configurations could for example involve, the number of stages in the multi-stage compressors, the number of trays in the separation units, the dimensions of reactor tubs and the reactor heat configuration. However, these optimisations are not always straight forward. Balances of increased operational cost, due to more energy needed, in

contrasts to decreased capital costs in the form of decreased number of trays or stages, needs to be evaluated more extensively to find a minimum in costs at good performance.

5 Cost Estimations

The cost estimation of the project involves both capital cost (CAPEX) and operation cost (OPEX). The CAPEX is estimated by using purchase equipment cost (PEC) as a base value with additional mark-up, arriving at a total capital investment (TCI). The OPEX is estimated for every major segment of the e-methanol project, separately. This is because different methods of estimation are used. Analysis of CAPEX, OPEX and revenues generated over the lifetime period of the project is later discussed and evaluated. A futuristic scenario was also analysed in order to look at the long-term feasibility of an e-methanol project of this size and configuration.

5.1 Financial Assumptions

The following financial assumptions were made:

- It is assumed that all capital costs are expenditures the first year.
- A conversion factor of 0.82 €/€ was assumed to convert the total operational costs. Based on the value of the currencies from January 2021⁵, before the effects of current inflation.
- An inflation rate of 1.33% was assumed, which is the mean value from the time 2015-2019⁵. The reasoning behind this being that the effects of the Covid-pandemic had unreasonable effects on normally expected inflation rates in years 2020-2022. Equation A5 in Appendix A was used for the calculations.
- A weighted average cost of capital (WACC) of 8% was assumed. The total rate consisted of two parts, 6% representing the cost of debt and 2% the cost of equity.
- It is assumed that all costs except the capital cost for the PEM electrolyser and the buffer system, are from 2018 and subjected to inflation which has been considered in the cost estimates.
- That oxygen is compressed to 200 bar and directly sold in bottles with a value of 150 €/ton. This value was assumed based on previous studies^{5, 62, 63} and was validated using an average market value of exported oxygen in Europe⁶⁴ (from 2021) of 0.2 €/Nm³ and a weight⁶⁵ of 1.4291 kg/Nm³.
- The selling price of methanol is assumed to be 400 €/ton which is a typical average market value in Europe⁶².
- Carbon credits are taken into consideration and are valued at 80 €/saved ton CO₂. The price of sold carbon credits are predicated to increase to a value of 130 €/ton by the

year 2030 and further to a value of 221 €/ton by the year 2040 as a result of further restrictions on carbon emissions⁵.

- It is assumed that there is a linear increase to the future values of carbon credits. The values for the linear regression can be seen in Appendix A.
- An industrial value associated with the PEM electrolyser provides by vendors of AFRY (March 2023) was used for the purchase equipment cost of the electrolysis plant.
- The electricity consumption of the compression system was not considered due to the difficulty of finding literature supporting the chosen compression model and pressure ratio. However, the effect of this exclusion was discussed.

5.2 Capital Costs

The capital cost (CAPEX) of the methanol synthesis-, carbon capture- and for the PEM electrolyser is estimated. The CAPEX for the compressors and buffer tanks is also estimated.

The purchase equipment costs (PEC) of the carbon capture and storage (CCS) plant and the methanol plant were calculated using Equations 5 and 6⁶²:

$$C_{CCS} = 2.403 * 10^3 * (M_{in})^{0.65} \quad \text{(Equation 5)}$$

$$C_{MeOH} = 12.783 * 10^3 * (M_{in})^{0.65} \quad \text{(Equation 6)}$$

Where C is the cost of equipment for the CCS-plant or methanol system, M_{in} is the mass flow rate of exhaust gas and reactants into the CCS-plant and methanol system, respectively. The exponential value of 0.65 was adopted as a normal scaling factor^{5, 42}. The estimated PEC for the CCS-plant and methanol system were in coherence with a report Concawe, Environmental Science for European Refining⁶⁶ and the simulation in Aspen Plus V.11, respectively.

Hydrogen and carbon dioxide are stored in buffer tanks whilst the oxygen produced in the electrolyser is directly compressed to 200 bar and bottled for selling. Equation 7 was used to calculate the PEC of the hydrogen-, oxygen- and carbon dioxide compressors^{5, 62}:

$$C = C_0 * (M_{in} * \ln\beta)^{0.65} \quad \text{(Equation 7)}$$

Where C is the purchase equipment cost and C_0 is the base parameter dependent on which gas is being processed (values adopted are 36856, 2651, and 2327 for H₂, CO₂ and O₂, respectively⁶². m is the mass flow rate and β is the compression ratio of the different gases, values⁶² used were 6.5 for H₂ and O₂ and 4.47 for CO₂. Adopting the same scaling factor of 0.65.

The PEC of the buffer tanks was estimated, to allow continues operation in case processes upstream went out of operation. By assuming a supply of raw materials from the buffer tanks for the duration of 5 hours, receptively 3 hours of continues operation, for CO₂ and H₂ respectively. CO₂ have a density of around 1103 kg/m³ at -25 °C hence a 36.26 m³ tank is needed with a specific cost⁵ of 8500 €/m³. A buffer tank with a capacity of 3800 kg H₂ costs around 600 k\$ including mark-up costs according to a vendor⁶⁷.

The total PEC is estimated to be 62% of the total capital investment (TCI)⁶² which covers the direct- and indirect labour associated with the material and installation of that equipment; contingencies, the cost of site preparation and building, engineering, construction expenses, land for the process equipment and working capital. The total TCI is equivalent to 169.64 M€, see Table 9.

Table 9: Shows a summary of the capital costs for e-methanol plant with a capacity of producing 46,000 ton/year. The capital cost for PEM electrolyser and buffer systems are not subjected to inflation since they represent values from 2023.

Unit/System	PEC (M€)
PEM Electrolyser	88
CSS System	2.50
MeOH System	5.09
Compressor System	8.20
Buffer System	0.31
Total Purchase Equipment Cost	104.1
Total (inc. inflation)	105.17
Total Capital Investment	169.64

5.3 Operational Costs

This section covers all operational expenditures associated with the e-methanol production plant. Under sections 5.3.1-5.3.4 tables of OPEX, for individual systems (methanol synthesis, electrolysis, and CCS-plant) and summary over the e-methanol plant, are displayed.

5.3.1 PEM Operating Costs

The OPEX of the PEM electrolyser was calculated using values generated from a Excel-template provided by National Renewable Energy Laboratory⁶⁸ (NREL) for centralised distribution of a PEM electrolyser with capacities up to production of 50,000 kg/day. These values are presented in \$, as provided by NREL, and converted to € using the assumed conversion of 0.82 €/\$, see Tables 10-11.

Table 10: Shows the fixed operating costs scaled, in accordance with the National Renewable Energy Laboratory⁶⁸, to the design capacity of a PEM electrolyser producing 1204 kg/h. The costs are directly imported from the Excel-template provided by NREL and presented € using the conversion factor of 0.82 €/.\$.

Fixed Operating Costs	Specific Cost	Cost (€/year)
Total plant staff	10	
Staff working hours/year	2080	
Burdened labor cost, including overhead (€/man-hour)	€41	€852 800
G&A rate (% of labor cost)	20%	€170 560

Property tax and insurance rate (% of total capital investment per year)	2%	€820 913
Material costs for maintenance and repairs (\$/year)		€862 831
Planned Replacement Cost of Stack	15% of direct capital costs every 7 th year	13.2 M€
Unplanned replacement cost		€49 806
Total Fixed Operating Costs		€2 707 105

Table 11: Shows the fixed operating costs scaled, in accordance with the National Renewable Energy Laboratory⁶⁸, to the design capacity of a PEM electrolyser producing 1204 kg/h. The costs are directly imported from the algorithm provided by NREL and presented in € using the conversion factor of 0.82 €/\$.

Cost basis for Feed and Utilities	Cost (€/year)
Process Water Price: \$/gal \$0.002375; Usage per kg H ₂ : 3.78 gal	€147 256
Industrial Electricity in PEM: Price in Startup Year (\$2016)/kWh: 0.069980611; Usage (kWh/kg H ₂): 55.5	€36 818 436
Total Variable Operating Costs (€/year)	€36 965 693

5.2.2 CSS Operating Costs

The OPEX for the CCS-plant are based on the consumption of MEA-solvent and the general power consumption. The values used for estimating the specific costs of MEA and power consumption of carbon capture are displayed in Table 12.

Table 12: Shows the operating costs for a CCS-plant with the capacity to provide the methanol system with 8000 kg/h of captured CO₂. Values in this table is calculated using parameters from Table 6.

Solvent Replacement Cost	0.1824 M€/year
Power Consumption	1.3862 M€/year
Total Operating Cost	1.5686 M€/year

5.3.3 Methanol System Operating Costs

The OPEX of the methanol synthesis system is based on the value presented by the Aspen Plus simulation. This value accounts for the electricity and utilities, the operational labour, maintenance cost, operational charges, and plant overhead, see Table 13.

Table 13: Shows the operating costs for the methanol system. Were power consumption accounts for around 0.54 M€/year of the operating costs.

Methanol System Cost	M€/year
Operating Costs	3.35
Catalyst Consumption	2.91

5.3.4 Operation Cost Summary

The total OPEX of the e-methanol plant is summarised in Table 14.

Table 14: Shows a summary of the operational costs for a e-methanol plant with a capacity of producing 46,000 ton/year. Inflation applies to all operating costs and adds up to a yearly cost of 50.74 M€ and 64.84 M€ on a normal year of operation and each seventh year of operation, respectively.

OPEX Origin	OPEX (M€/year)
PEM Variable Operating Costs	36.97
PEM Fixed Operating Costs	2.70
PEM Fixed Operating Costs (each 7 th year)	15.9
Total OPEX PEM	39.67
Total OPEX PEM (each 7 th year)	52.87
OPEX MeOH	6.26
OPEX CCS	1.57
Total (Normal, inc. inflation)	50.74
Total (every 7 th year, inc. inflation)	64.84

5.4 Revenues

The revenues of this e-methanol project are estimated using production rates, and the market value prices at which products and by-products are sold, see Table 15.

Table 15: Shows the annual revenues expected in a start-up year of 2023, using estimations of current market values for oxygen, methanol, and projected market values for carbon emission credits.

Product	Revenue (M€/year)
Oxygen	11.56
Methanol	18.4
Sold Carbon Emission Credits	5.12
Total	35.08

5.5 Cost Analysis

The cost analysis of this project used two different methods for generating results of profitability over the lifetime of the project and for evaluation of minimum methanol pricing:

- The first one being the net present value (NPV) of the project's annual cashflows, calculated by setting a fixed current- and futuristic market price at which methanol is sold. See Equation 8.
- The second method being calculating the levelized cost of methanol (LCoM) which states the market selling price of methanol to achieve a NPV equal to zero. This is the price methanol needs to be sold at in order to reach break-even at the end of this project's lifetime, see Equation 9.

$$NPV = \sum_{t=0}^{20} \frac{(CAPEX_t + OPEX_t) - (RO_t + RCC_t)}{(1+r)^t} \quad (\text{Equation 8})$$

$$LCoM = \frac{\sum_{t=0}^{20} \frac{(CAPEX_t + OPEX_t) - (RO_t + RCC_t)}{(1+r)^t}}{\sum_{t=0}^{20} \frac{P_t}{(1+r)^t}} \quad (\text{Equation 9})$$

Where $0 \leq t \leq 20$ representing a current year during the plants operating lifetime. $CAPEX_t$ is the capital cost during year t . However, all capital costs are expected to be financialised during the first start-up year. The $OPEX_t$ are the operating costs during that year. RO_t and RCC_t being the revenues from sold oxygen and carbon credits. Finally, r is the WACC and P_t is the production of methanol each year.

The yearly cash flows and the accumulated NPV at the end of the project lifetime are displayed in Figure 12 and 13.

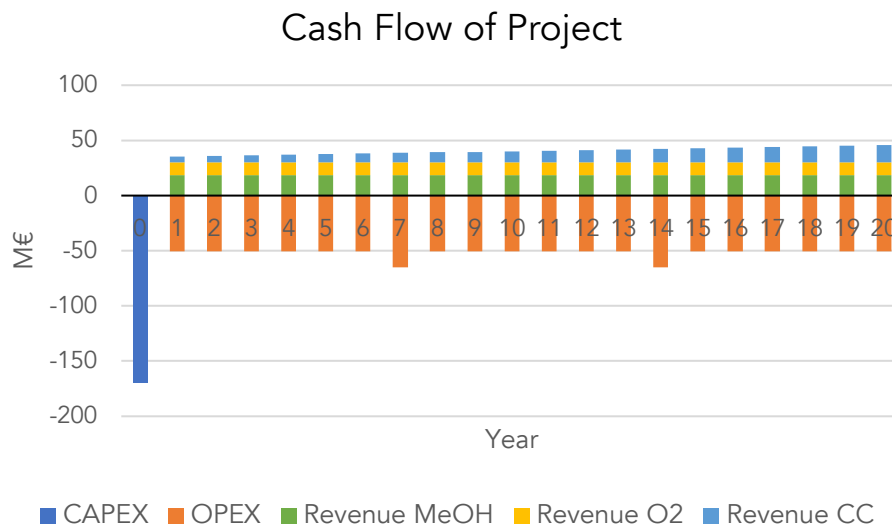


Figure 12: The yearly cash flows generated by the e-methanol plant during the project's lifetime of 20 years without the use of WACC.

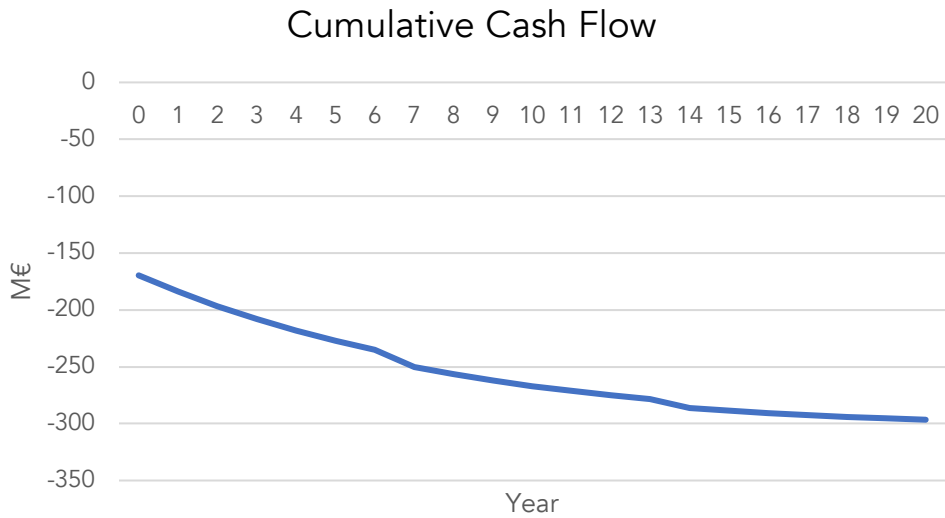


Figure 13: The development of NPV during the lifetime of the project.

The accumulated NPV was calculated to -296.56 M€, which indicate the unfeasibility of e-methanol production especially if the methanol is sold at the same market price as fossil-based methanol (at 400 €/ton). To get a better understanding of the cost distribution and largest contributors to the negative NPV, see Figures 14 and 15.

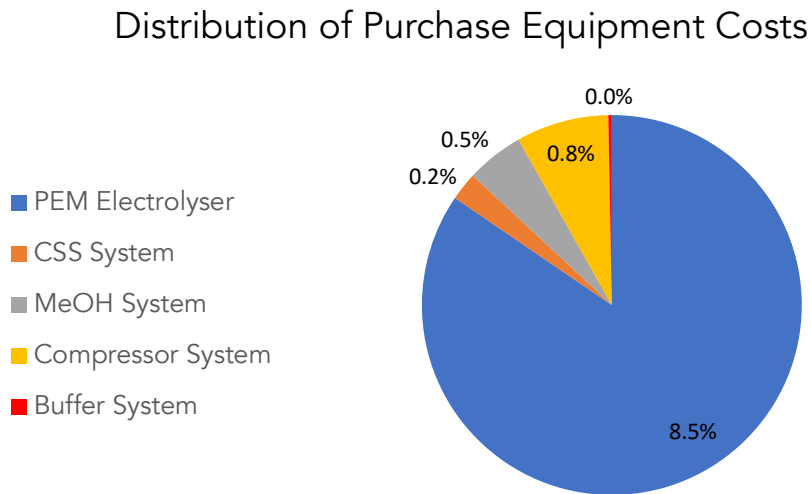


Figure 14: Shows the distribution of purchase equipment cost for the operational units of an e-methanol plant with a capacity to produce 46,000 ton/year.

Distribution of Operational Costs

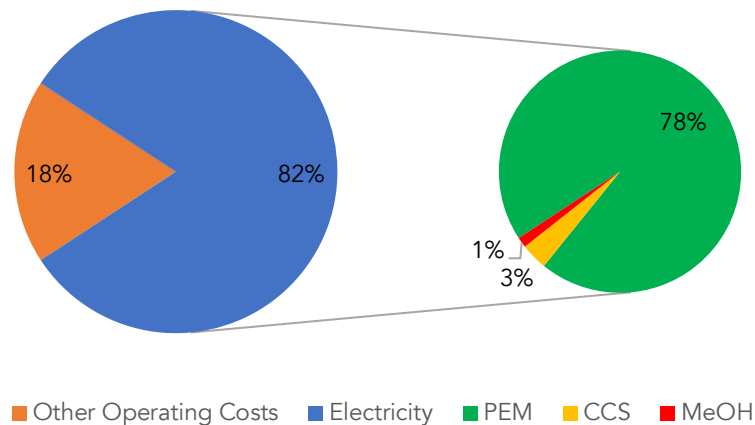


Figure 15: Shows the operational cost distribution a normal year of operation on an e-methanol plant with a capacity to produce 46,000 ton/year, not considering every 7th year. The electricity consumption for the methanol system is given by Aspen Plus V.11 at a rate of 82.1629 \$/h. The electricity for compression systems and buffer system are not taken into consideration and assumed neglectable.

The largest contributor to the negative NPV is the PEM electrolysis in terms of capital cost and operational costs, with a contribution of 84.5% to the total purchase equipment costs coupled with a majority of the electricity consumption.

The levelized cost of e-methanol was calculated to 1040.73 €/ton which is around two and a half times more expensive than the market value of methanol (400 – 450 €/ton)⁶⁹, conventionally produced from fossil-based derivatives. This value is validated by the results of other studies^{5, 41}. This highlights the unprofitable nature of a large-scale e-methanol production and confirms that production of e-methanol is yet not competitive with other methods of methanol production. However, it should be noted that the methanol market is increasing consequently by increased demands in future years. Therefore, methanol prices are expected to increase as a combination of both increased demand and increased price of carbon emission credits. To further strengthen the position of e-methanol production, price of electricity as well as advancement of technologies provides better efficiencies which will make the price of e-methanol more competitive in comparison to conventional fossil-based methanol.

5.5.1 Futuristic Scenario

To further elaborate on the possibilities of a profitable future for e-methanol production, a futuristic scenario was analysed. Concluding that for the time being, it has shown to be unprofitable to produce e-methanol of this scale. However, for a futuristic evaluation of e-methanol production, four variable parameters can be taken into consideration:

- The market value of 400 €/ton methanol best represents the market value of methanol in the Asian region whilst regions like the US have market prices of methanol closer to 500 €/ton⁷⁰. Taking a high-end market value of methanol, the increased demand and general forecasted market value of methanol into account, coupled with the predicted

increased value of fossil-based methanol due to strengthened European policies towards carbon emissions⁵, a futuristic value of around 550 €/ton was analysed⁷¹.

- The market value of bottled oxygen can also be predicted to increase based on the increasing demand. The oxygen market is forecasted to increase to 9.4 billion dollars in 2026, in comparison to 4.4 billion dollars in 2018. With the increasing demand, an assumed price of bottled oxygen in tubes could potentially be 200 €/ton⁶⁹.
- The technological advancement of electrolyser technologies providing higher efficiencies and lower capital cost. For example, the advancement of SOEC technologies providing higher efficiencies and lower capital cost in comparison to PEM electrolysis. An assumption of 15% decreased in total capital investment coupled with 7% increased efficiency (in terms of energy consumption (kWh) per produced kilogram of hydrogen) can be assumed for futuristic scenarios. Using a value⁷² of 51.7 kWh/kg H₂ and TCI of 144.19 M€.
- Lastly, the electricity price can be assumed to decrease with the development of renewable sources. Taking, both an increase in the grid capacity and the efficiencies of these renewable sources, into account. A futuristic electricity price⁷² of 0.03 \$/kWh, equivalent to 0.0246 €/kWh using the conversion factor of 0.82 €/\$, was assumed.

Assuming electricity consumption representing 97% of the operating variable cost and fixed operating cost representing 31% of the total operating cost for an e-methanol plant⁵, the electricity consumption contributes to around 67% of the total operating costs. Other assumptions include a fixed carbon credit value of 221 €/ton and that the fixed variable cost remained the same, considering that the variable operating costs was the largest contributor to the total operational costs. Futuristic cost reductions and revenues are summarised in Table 16 and the NPV of a futuristic e-methanol plant producing 46,000 ton/year is seen in Figure 16.

Table 16: A summary of the futuristic revenues and reduced costs for an e-methanol plant with a capacity of producing 46,000 ton/year.

Variable Operating Cost Electrolysis	12.63 M€/year
Revenue MeOH	25.30 M€/year
Revenue O ₂	14.41 M€/year
Revenue CC	14.14 M€/year
TCI	144.19 M€

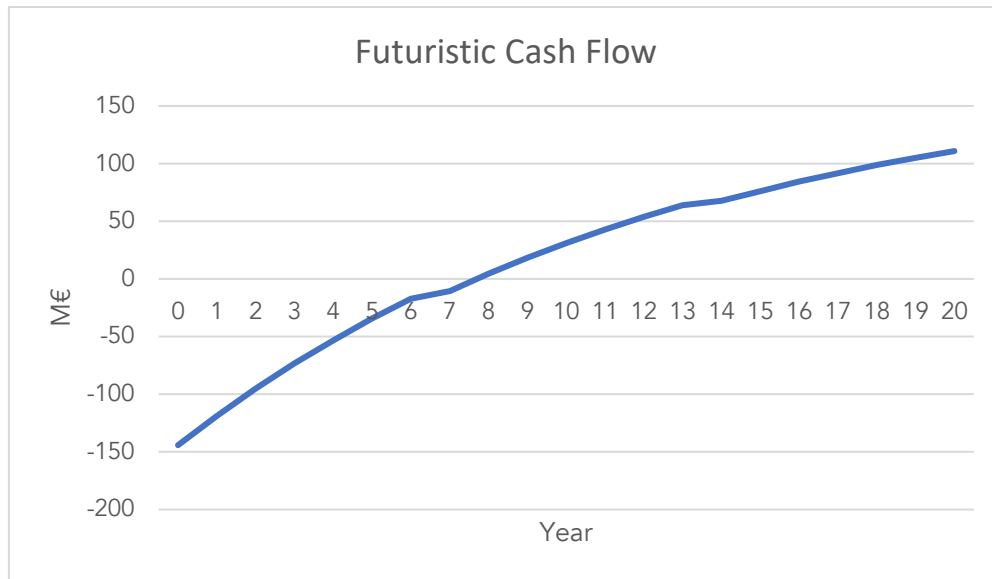


Figure 16: Shows the cumulative cash flow over the project lifetime (NPV) in a futuristic scenario with increased methanol-, oxygen and carbon credit prices. Coupled with higher electrolysis efficiencies and reduced electricity price.

A futuristic scenario proved that the production of e-methanol was profitable. It generated a highly positive net present value (NPV) of 110.89 M€ after the project lifetime. With a break-even time somewhere in between year 7 and year 8. This showcases the profitability of investments and the potential performance of technologies within the production of e-methanol.

5.5.2 Economical Discussion

Evaluating near- and long terms investments in e-methanol shows that projects of this configuration and capacity are unfeasible in the near term much due to the inefficiencies of electrolysis. For the time being there are no other technologies with high enough technical readiness level to compete with the PEM electrolyser hence this technology being the only viable solution for e-methanol production via direct CO₂-hydrogenation. However, with the optimistic estimations in a futuristic scenario, the production of e-methanol of this capacity and configuration showed to be extremely feasible in the long term. There are currently few e-methanol plants operational on the market today, which enables early adopters to enter a relative non-competitive market landscape. This provides opportunities for companies to acquire large market shares and establish operations in view of a profitable future, which essentially is the trade-off for the present unprofitability today.

It is worth mentioning that these results do not take all material costs into consideration. For example, pipelines and equipment capable of handling hydrogen that minimises the risk of hydrogen embrittlement, are more expensive than ones accounted for. Additionally, some financial parameters such as senior debt, equity and working capital, that realistically is accounted for in these types of projects, are not considered. Hence increasing the costs of projects of this configuration and capacity.

Operating costs for the compression of hydrogen was not taken into consideration in the cost estimates. Therefore, it is safe to assume that the operating costs will be slightly higher.

Compression of hydrogen is more expensive in comparison to carbon dioxide and oxygen. The average power consumption, compressing hydrogen from ambient pressures to 200 bar, is approximately 2 – 5 kWh/kg of hydrogen⁷³. Using the average industrial electricity price of 57.8 €/MWh, the production flow of 1204 kg/h and 8000 hours of operation, the annual cost of hydrogen compression would be around 2 M€. This, in addition with the OPEX for compression of oxygen and carbon dioxide, is very small amount in comparison to the total operating costs. Therefore, this would not affect the results significantly.

An assumed selling price of bottled oxygen was assumed to 150 €/ton which is in line with the average price of exported oxygen (0.2 €/Nm³) in Europe from 2021⁶⁴ and the density of 1.4291 (kg/Nm³)⁶⁵. Furthermore, the possibility of selling oxygen directly as medical oxygen has been studied by Maggio, G. et. al.⁷⁴, suggesting that oxygen selling prices could go up to 3000 €/ton which would have a significant impact on the profitability of an e-methanol plant. However, the purity of the oxygen gas for medical purposes needs to be at least 99.5 v/v % according to WHO⁷⁵. Realistically, the oxygen produced from electrolysis has a purity⁷⁶ <99.5% and often needs to be treated in various ways before meeting high enough standards for export. Therefore, it is safe to assume that additional equipment for oxygen treatment- and bottling/tubing increases the CAPEX and OPEX. This increase was not estimated in this project and needs to be evaluated for in further work. Additionally, if proven to be feasible to directly sell produced oxygen as medical oxygen, further evaluations of profitability are needed to be done.

The WACC, used for the cost estimations, is likely to small. The cost of debt, assumed to 6%, is generally accepted. However, the cost of equity of 2% is probably too low. Shareholders and investors of these kind of projects typically wants a greater rate of return for their investment. Therefore, it is reasonable to assume a higher WACC in future projects. A higher WACC would affect the discounted cash flow of the project by increasing the NPV and the LCoM. Cost of equity is a difficult parameter to estimate, and companies must evaluate several parameters such as volatility, interest rate etc. Further evaluation of the cost of equity needs to be done in further work.

Finally, the TCI of the e-methanol plant is in the likelihood of being too small. The cost estimation used an installation factor of around 1.61, based on studied literature, to arrive at a TCI. However, according to other sources of literature the installation factor should be in the range of 2.5 – 5 for cost estimation of chemical engineering projects⁷⁷. For further evaluation of the feasibility of large-scale e-methanol production, a Lang method of approach could be appropriate. In order to get more accurate estimations, it is always beneficial to ask vendors for quotations hence minimising the amount of process- and installation cost that needs to be estimated.

6 Sensitivity analysis

A sensitivity analysis was made in order to determine which of the following five parameters that effected the net present value (NPV) the most. In this analysis the methanol selling price was fixed to the value of the levelized cost of methanol (LCoM) of 1040 €/t. These parameters were varied with a ±10% variation from their reference values. The parameters considered are electricity price, oxygen selling price, carbon emission credits, total capital investment and energy consumption per produced kilogram of hydrogen.

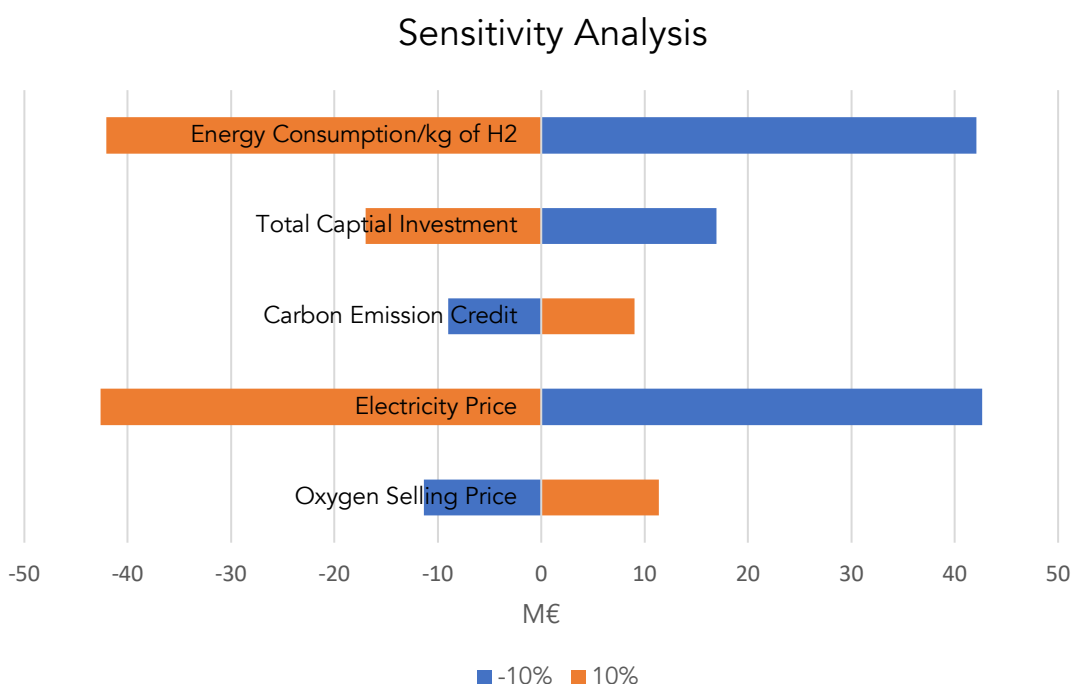


Figure 17: Shows the effect that a $\pm 10\%$ variation of five parameters have on the NPV.

The sensitivity analysis showed that a variation of electricity price and energy consumption per kilogram of hydrogen resulted in significant changes on the net present value (NPV) at the end of the project's lifetime. Both of these variations resulted in an increase, as well as a decrease, in profitability of around 40 M€ accumulated over 20 years. In the futuristic scenario these parameters were changed along with market prices of products and carbon emission credits. However, since the NPV showed the largest sensitivity towards changes in electricity price and energy consumption per kilogram of produced hydrogen, development and advancement in technologies governing these parameters may be enough to governing these parameters may be enough for making production of e-methanol profitable. Especially since 82% of the total operating costs originates from electricity and around 90% of the electricity consumption originates from the PEM electrolyser, in this case. Additionally, advancements of electrolysis technologies can correlate to decreased capital investment for equipment as well, further influencing the profitability.

7 Conclusion

Best suited technologies involved in e-methanol production, via direct CO₂-hydrogenation, proved to be hydrogen production via a proton-exchange membrane water electrolyser (PEM) mainly due to its capability of operating under intermittent power supply and post-combustion carbon capture, using MEA, due to its technical readiness level. Mechanical compressors were the only compressors capable of handling large enough mass flows and were therefore assumed to be the only option for operation. Finally a quasi-isothermal tubular reactor was best suited for methanol synthesis due to superior temperature control.

The operational- and financial estimations for a e-methanol plant with a capacity for production of 46,000 ton/year showed to be economically unfeasible with current technologies, price of equipment, price of utilities and market values of products. The net present value (NPV) at the end of the project lifetime proved to be negative 296.56 M€ and the levelized cost of methanol i.e. the price at which e-methanol needs to be sold at in order to break-even at the end of project lifetime, was 1040 €/ton. This is around 2.5 times more expensive than the current market value of fossil-based methanol.

A sensitivity analysis showed that the power consumption per produced kilogram of hydrogen in the PEM electrolyser (55.5 kWh/kg H₂) and the current price of industrial electricity (0.057 €/kWh) had the greatest impact on the net present value of the project at the end of the project lifetime period. Therefore, technological improvements resulting in reduction of these parameters will have the greatest impact on the future profitability of power-to-methanol projects.

However, an analysis of a futuristic scenario where four variables were changed according to futuristic forecasts and optimistic evaluations of advancements in technologies. This showed that investments in e-methanol projects showed to be very profitable and therefore feasible as an alternative green pathway for production of methanol over fossil-based production.

There are few e-methanol plants currently operational, which provides opportunities for early adopters to make early entries in the market. This enables companies to acquire large market shares in view of the future profitability.

This confirms the increasing interest in e-methanol production technologies and that the development of these technologies in the near future will offer opportunities for the decarbonisation of the heavy transport- and industry sector in view of a green energy transition towards net zero carbon emissions.

7.1 Further work

Due to the contradicting results of several studies regarding the kinetic models involved in the methanol synthesis, especially regarding the effects of CO-hydrogenation, further work is needed to conclude whether that reaction pathway should be included in methanol synthesis via CO₂-hydrogenation. This requires better understanding of how the different catalytic species interact with the reacting species in order to derive better suited kinetic models for methanol synthesis.

A lot of high purity water is produced from the methanol synthesis loop that can be taken advantage of via a recirculation back to the electrolysis, considering the high consumption of water in the production of hydrogen. This integration would add further sustainability to the production of e-methanol. However, this process integration needs to be evaluated based on the amount of water treatment that needs to be done to have enough purity of the recircled water to be able to re-enter the electrolytic cells of the electrolyser.

Finally, both TCI and WACC are likely to small, in turn generating unreasonably profitable results. Therefore, further evaluation of these parameters in the economic analysis needs to be done.

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Appendix A

$$\text{Selectivity} = \frac{\text{Produced desired product out of the reactor}}{\text{Consumed reactant in the reactor}} * \text{Stoichiometric factor} \quad (\text{Equation A1})$$

$$\text{Conversion} = \frac{\text{Consumption of reactant in reactor}}{\text{Reactant fed to the reactor}} \quad (\text{Equation A2})$$

$$\text{Yield} = \frac{\text{Desired product produced}}{\text{Reactant fed to the reactor}} * \text{Stoichiometric factor} \quad (\text{Equation A3})$$

$$C = C_0 \left(\frac{P}{P_0} \right)^f \quad (\text{Equation A4})$$

The C and C_0 represents the cost of the plant considered in this project and the cost of the reference plant from the literature, respectively. The P and P_0 are comparison parameters of the simulated and reference plant, the nature of which depends on the type of plants and the size of them. The f is a dimensionless scaling factor.

$$FV = PV * (1 + IR)^n \quad (\text{Equation A5})$$

The future value of (2023) is calculated using the present value (of 2018) times the sum of 1 and the inflation rate to the power of the number of years that has passed.

Table A1: Shows the values used for the linear regression of the forecasted carbon credit price.

X (year)	Y (€/t)
2023	80
2030	130
2040	221

Table A2: Shows the regression results of the carbon credit price expressed in equation $y=kx+m$, where y = carbon emission credit price and x = year.

k	m
8,349	-16813,79