Techno-economics of CCU pathways starting with carbon-rich streams

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by

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Abstract

Emissions of greenhouse gases (GHG) are the main cause of climate change, with as effect a rise in global temperature. The culprit in these emissions is carbon dioxide (CO_2). Carbon capture and utilization (CCU) can mitigate a part of these emissions, by converting carbon species to useful products. The typical route for CCU involves: carbon capture, compression, transportation and utilization.

This thesis takes on a slightly different approach. Instead of utilization at a centralized location, the utilization of carbon species will be realized on location. This is beneficial, since no transportation of CO_2 is required. Three different high partial pressure carbon sources will be addressed: tail-gas (TG) from steam methane reforming, blast furnace gas (BFG) from the steel industry and biogas from the bacterial degeneration of biomass. Each of these gas streams are composed of up to 50-60 mol % CO_2 and or CO. By capturing the carbon species in these gases or removing some of the inert components, different ratios of CO_2, CO, H_2 and inerts can be obtained. Electrolysis technologies will be used to upgrade the captured gases, with the addition of hydrogen or by adjusting the CO/CO_2 ratio. The electrolysis technologies considered are PEM and SOEC. The advantage of electrolysis is the potential for integration with renewable energy sources such as, wind, solar and hydro power. Depending on the electrolysis technology and carbon source, syngas with CO/CO_2 ratios varying between 0-4 can be obtained. Five different cases were defined with CO/CO_2 ratios equal to 0, 0.25, 1, 3 and 4. The upgraded syngas can then be used in the conversion towards several liquid fuels, such as methanol and Fischer-Tropsch (FT) liquids. Both methanol and FT liquids require a stoichiometric ratio of at least 2. For these two product routes a techno-economic analysis was performed.

As a first production route, methanol synthesis was discussed. The feasibility for each of the five cases was assessed, by comparing the cost price of the methanol with the respective market price. A reference methanol plant from literature was implemented in Aspen Plus to obtain the energy and mass balances for each case. The mass balances showed the amounts of hydrogen and carbon species required to produce one ton of methanol. The total cost price of the methanol consists of the operational expenses (OPEX) and capital expenses (CAPEX). The OPEX reflects the costs required to run the process. This includes the prices for the feedstock and labour costs for example. The CAPEX consists of the capital investments. Based on the CO/CO_2, Case 3 with $CO/CO_2 = 4$, should be the cheapest case as less hydrogen has to be added to produce one ton of methanol. However, Case 4 with a $CO/CO_2 = 0.25$ is the cheapest option. Case 4 originated from the TG stream, which already had a high fraction of H_2 present in the TG. Therefore, Case 4 requires less addition of hydrogen. Capture costs were also lower in Case 4, compared to the other cases. At a market price for methanol of €400 per ton, a maximum electricity price of €30 per MWh was allowable.

FT liquids were overall found to be an unfeasible product, when considering renewable production of hydrogen and CO from CO_2 electrolysis. In FT liquids, waxes (C_{20+}) are a requirement in the product fraction as these can be sold at the highest price. When considering the production of gasoline and diesel, the renewable FT route proved to be unfeasible. In general it was found that for each case, irrespective of product, more than 50 % of the product cost price, was included in the costs for electrolysis. And as the electrolysis technologies require electricity to operate, it can be concluded that electricity is the determining factor.

Preface

During my BSc Mechanical Engineering at the Delft University of Technology, I was unsure about what MSc track interested me the most. It was only during my BSc final project under the supervision of Professor Vlugt and Peter van den broeke, that my interest in the MSc track Energy Process Technology was sparked. As a result I started my MSc Energy & Process Technology in 2017, a decision I have not regretted ever since.

This thesis was written to fulfil the graduation requirements of the Energy and Process Technology track in the Mechanical Engineering MSc program at the Delft University of Technology. In this thesis the techno-economics on the feasibility of CCU processes will be discussed, based on renewable production of resources. With this thesis I wanted to investigate how some existing production routes, could be altered to make them sustainable. In my future career, I hope to continue to contribute on improving the sustainability of processes.

I would like to thank Professor Vlugt and Mahinder Ramdin for their weekly feedback during this thesis and participating in my graduation committee. Special gratitude to Peter van den Broeke for being my daily supervisor and his guidance during this thesis. Peter was always available for a discussion, which usually led to new insights. Also many thanks to Professor Urakawa and Ahmadreza Rahbari for participating in my graduation committee. Lastly I want to thank Andrea Arecco, for the work we did together and the support.

J.A.C. Tanke
Delft, May 2020

Contents

Nomenclature

bbl	Barrel of oil
BE	Break-even
BFG	Blast furnace gas
CAPEX	Capital expenditure
CCS	Carbon capture and sequestration
CCU	Carbon capture and utilization
DAC	Direct air capture
ECR	Electrochemical CO_2 reduction
FE	Faradaic efficiency
FT	Fischer-Tropsch
GHG	Green house gases
GtL	Gas-to-Liquids
HHV	Higher heating value
HTFT	High temperature Fischer-Tropsch
LHV	Lower heating value
LTFT	Low temperature Fischer-Tropsch
NGL	Natural gas liquids
OPEX	Operational expenditure
P2C	Power-2-chemicals
PC	Power consumption
PEM	Proton exchange membrane
POX	Partial oxidation
PSA	Pressure swing adsorption
RWGS	Reverse water-gas shift
SG	Syngas
SMR	Steam methane reforming
SOEC	Solid oxide electrolysis cell
TG	Tail-gas
WGS	Water-gas shift

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Introduction

Emissions of greenhouse gases (GHG) are the main cause of climate change, with as effect a rise in global temperature. The culprit in these emissions is carbon dioxide (CO_2). The major part of these emissions is caused by the use of fossil fuels to generate heat and power. Over the last century emissions of GHG have strongly increased. As an illustration, annual carbon dioxide emissions have risen from 6 billion tons in 1950 to 35 billion tons in 2013 [50]. To counteract this increase in GHG emissions and to address severe weather events (hurricanes, heat waves, and flooding) associated with the global climate change, a reduction in CO_2 emissions must be realized. Therefore, a range of sustainable solutions addressing these issues are being developed.

One of the solutions to tackle this problem is to use carbon capture and utilization (CCU). Through CCU, CO_2 is captured, which can then be used in a next step as feedstock for the synthesis of different chemicals. This is different from carbon capture and sequestration (CCS), in which the CO_2 is captured and typically stored underground. The CO_2 can be captured from different sources, such as flue gas, a range of off gases like tail-gas (TG) from steam methane reforming (SMR) or blast furnace gas (BFG) from steel industry and from the air through direct air capture (DAC). An emerging technology to utilize this CO_2 is through power-2-chemicals (P2C) processes. Typical examples include hydrogenation reactions of CO_2, such as methanol synthesis and methanation. Besides P2C, there are also options that can convert syngas to liquid fuels called gas-to-liquid (GtL) processes, for example Fischer Tropsch (FT) synthesis. Using FT synthesis, CO and H_2 are converted to a range of different molecules with increasing carbon atoms. Another process that allows the utilization of CO_2 is electrochemical CO_2 reduction (ECR). ECR makes use of the electrocatalytic conversion of CO_2 to products. However, this will be discussed briefly in Appendix A, as ECR is still only available at lab scale.

For these P2C and GtL routes hydrogen is required and preferably from a non-fossil fuel source, as conventional hydrogen is produced through steam methane reforming (SMR). Water electrolysis is the preferred solution, to supply this demand for hydrogen, as it can be operated in conjunction with renewable energy sources (solar, wind or hydro power). Generally there are a number of water electrolysis technologies available, such as alkaline electrolysis, PEM electrolysis or SOEC electrolysis. With alkaline electrolysis being the most developed technology and SOEC the newest. SOEC is now being explored for co-electrolysis and CO_2 electrolysis applications, which opens up extra options for the production of syngas.

1.1. Problem statement

In this thesis different CCU pathways will be assessed based on the availability of carbon-rich feed streams. The focus lies on the conversion of CO_2 and CO to other chemicals, which will include the production of hydrogen by means of electrolysis. Existing CCU and CCS options involve the capture, compression, transportation and then utilization or sequestration of the CO_2 shown in Figure 1.1a [29]. This thesis will take on a different approach, adapted from Figure 1.1a, shown in Figure 1.1b, where captured CO_2 is utilized and distributed locally.

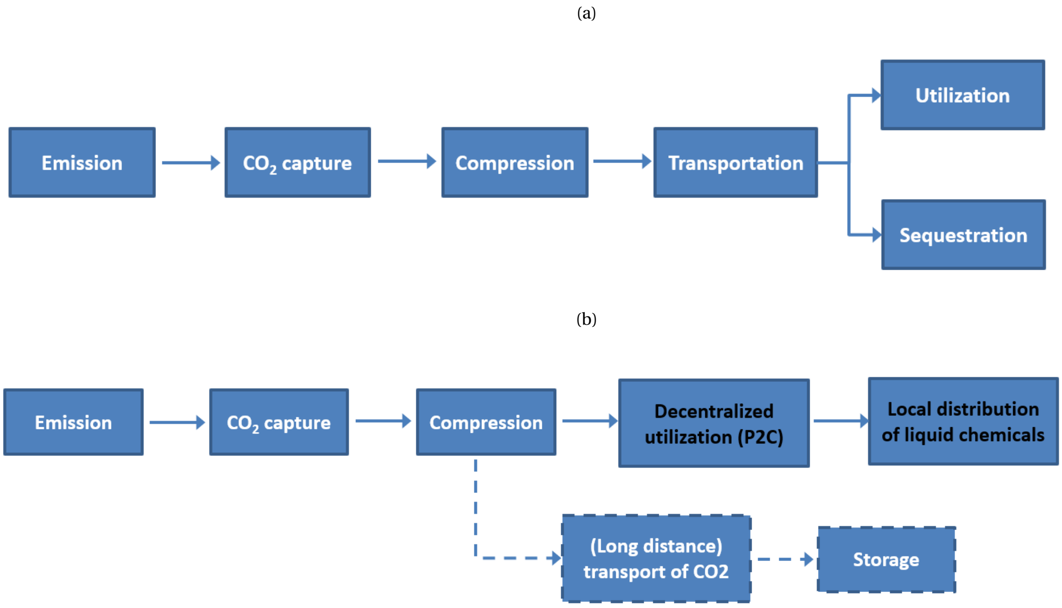

Figure 1.1: (a) Existing CCU and CCS route adapted from Hasan et al. (2014) [29] (b) Modified CCU pathway from Figure 1.1a that will form the basis of this thesis in which the CO_2 will not be transported and utilized, but utilized on the location of capture

The main goal is to identify which of the pathways will be most feasible in terms of technological and economic aspects. An initial indication will be given based on the marginal cost price analysis. This means that cost prices are calculated based on the feedstock costs and compared to the market price to assess if production is feasible [53].

1.2. Literature overview

The main idea is to capture CO_2, upgrade the captured CO_2 using PEM/SOEC electrolysis and convert this syngas to products. These steps are schematically shown by the blocks in Figure 1.2. By using water electrolysis, CO_2 electrolysis and co-electrolysis, the syngas can be adjusted to different compositions. For both syngas upgrading and synthesis processes, heat and renewable electricity need to be supplied. In the remainder of this introduction, these different steps will be investigated in more detail based on a brief literature overview.

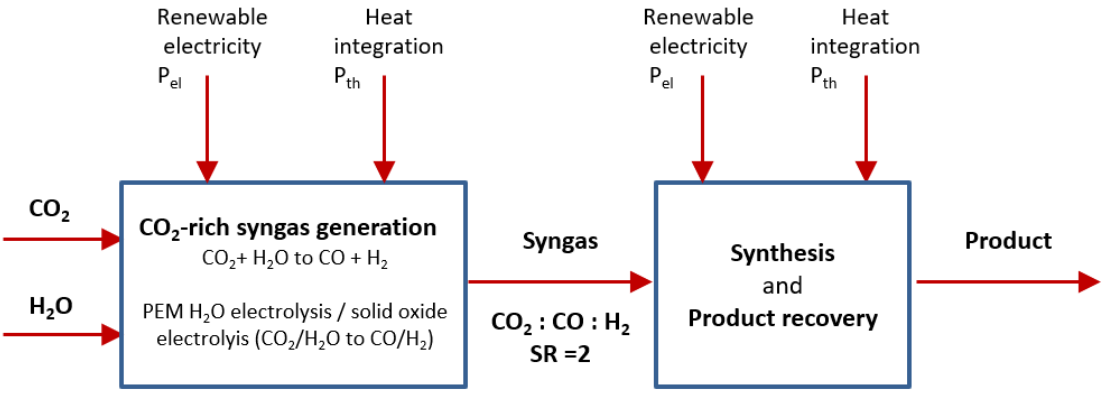

Figure 1.2: Schematic representation of the relevant steps that will be discussed in this thesis. Captured CO_2 is upgraded using electrolysis technology. The syngas that is obtained can be converted to a range of products. For both syngas upgrading and conversion process, heat and renewable electricity is required.

1.3. Carbon capture and utilization (CCU) pathways

There are different sources that contribute to the emission of CO_2. In 2019, 30% of global emissions could be contributed to coal-fired electricity generation (10 Gton) [32]. Therefore, carbon capture methods in conjunction with CCU, can prove to be useful to reduce CO_2 emissions. Typical carbon capture methods that can be distinguished are: post-combustion carbon capture for flue gas treatment (power, steel and cement plants), high partial pressure CO_2 sources like SMR for H_2 production or biogas from biomethane and direct air capture (DAC) [45, 55, 61].

Post-combustion capture

The process for CO_2 capture after the combustion of fossil fuels is called post-combustion CO_2 capture. This involves the capture of CO_2 from flue gas for example, which contains between 10-15wt% CO_2 [3, 25, 43]. Flue gas is typically captured by means of chemical absorption. Chemical absorption capture technology is based on the absorption of CO_2 on amine solvents [59].

The steps in the absorption process are as follows: (1) First the flue gas is treated and desulphurized (if necessary), (2) then the CO_2 is absorbed on the amine solvent and (3) finally regenerated using steam to separate the CO_2 from the solvent. Table 1.1 shows regeneration energy requirements and capture rates for different flue gas streams as found in literature.

Table 1.1: CO_2 mass fraction, capture energy requirement and capture rate for amine absorption processes based on different literature sources

CO_2 mass fraction [wt%]	Regeneration energy [GJ/t_{CO_2}]	Capture rate [%]	reference [-]
12	2.1 - 3.5	90	[25]
13	3.6	90	[3]
14	3.5	90	[43]
14	3.2	85	[59]
10 - 15	3.0	90	[6]

High partial pressure carbon streams

A second group of carbon sources can be categorized as high partial pressure streams. This group includes gas streams such as tail-gas (TG) from SMR, blast furnace gas (BFG) from steel production and biogas from the bacterial degradation of biomass. This thesis will focus on these carbon-rich gas streams and the usage in the CCU chain. The SMR TG typically contains a carbon fraction between 50-60 mol%, which is significantly higher than post combustion sources [54]. An interesting option is shown in Figure 1.3, which is an adaptation of the conventional SMR process. In the conventional SMR process, the tail-gas is burned and used to generate heat, which is integrated in the process. Whereas in the adapted process the tail-gas is treated and used in the CCU process chain.

The different steps in the adjusted SMR process to produce hydrogen are as follows:

1. The conversion of methane with steam through SMR, which produces a syngas with H_2/CO equal to 3 according to Eq. 1.1. This is combined with water-gas shift (WGS) reaction shown in Eq. 1.2 to produce more hydrogen [54].

$$\text{SMR: } CH_4 + H_2O \longrightarrow CO + 3H_2 \tag{1.1}$$

$$\text{WGS: } CO + H_2O \longrightarrow CO_2 + H_2 \tag{1.2}$$

2. Pressure swing adsorption (PSA) is used to produce H_2 and remove impurities, which leaves a high partial pressure carbon tail-gas. Traditionally this tail-gas stream is used to generate heat for the SMR/WGS reaction. However, it has potential in the CCU process chain as well due to the high fraction of CO_2, CO and H_2.

3. The tail-gas is separated in the next step, leaving a CO_2-rich and CO_2-lean stream. The CO_2-lean stream can be used as substitute for the conventional tail-gas by burning the gas and generating heat for the SMR/WGS reaction.

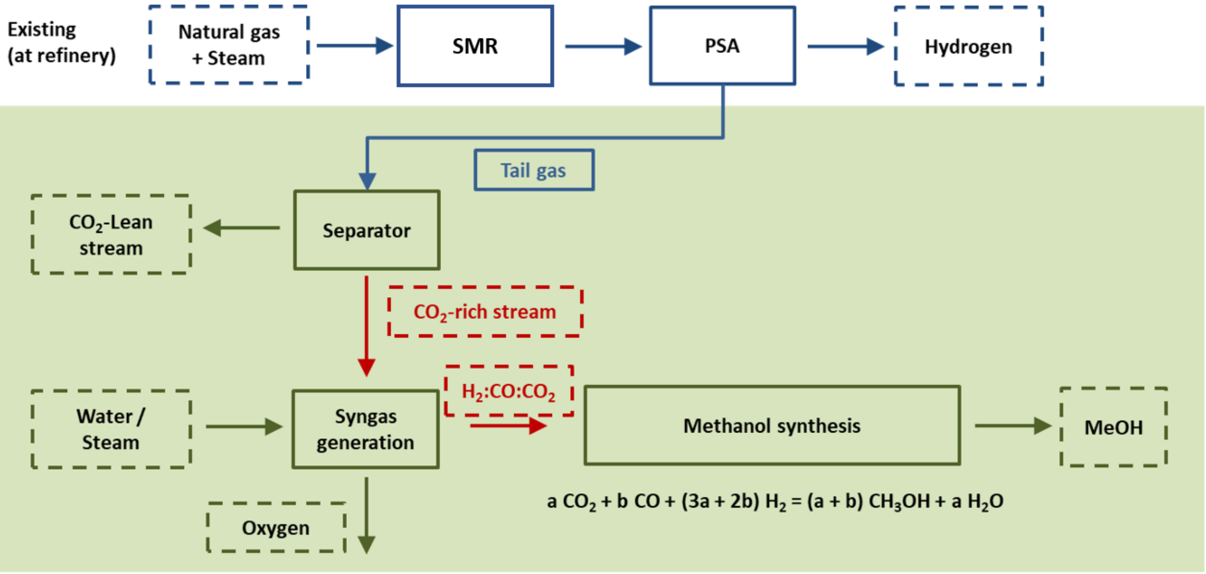

Figure 1.3: Adaptation, displayed by the green block, of an existing SMR (steam methane reforming) process to produce hydrogen. The PSA (pressure swing adsorption) step produces hydrogen and a rest stream called tail-gas. The tail-gas is separated into a CO_2-lean and rich stream. The CO_2-rich stream can be used in CCU processes when upgraded by the addition of hydrogen from electrolysis technology. This syngas can be used in the methanol synthesis process producing methanol (MeOH)

4. In the final step the CO_2-rich stream can be upgraded, by the addition of hydrogen from water electrolysis. The syngas can be converted to products such as methanol or other products, using a methanol synthesis reactor or other synthesis technologies.

Different technologies can be used to separate the CO_2 in step 3, such as PSA, amine absorption, membrane separation and cryogenic separation [34]. However, PSA is the most well established technology for tail-gas separation that makes use of the physical binding of gas molecules to adsorbent material. PSA works at constant temperature, and by alternating pressure and partial pressure, adsorption and desorption of the species are realized. In case of PSA two steps are required when applied in the SMR process, one for the capture of pure H_2 and a second PSA step for the capture of the CO_2 from the TG [54]. The composition of the tail-gas is given in Table 1.2. A big advantage of the TG is the presence of hydrogen, which benefits CCU processes like methanol synthesis, discussed in Figure 1.3, by lowering the required hydrogen addition.

Table 1.2: Typical mol fractions for tail-gas, blast furnace gas and biogas from industry containing high fractions of carbon species.

	CO_2 mol%	CO mol%	H_2 mol%	CH_4 mol%	N_2 mol%	carbon fraction mol%
Tail-gas	40-45	9-12	27-28	12-20	2-3	**49-57**
Blast furnace gas	20-25	20-25	5-10	0	40-45	**40-50**
Biogas	25-50	0	0	50-75	0	**25-50**

Besides TG there are other sources containing high partial pressures of carbon species. A second option is blast furnace gas, which is produced during the steel manufacturing process. The BFG is traditionally used to generate heat, but can also be utilized as feedstock in P2C and GtL processes. BFG contains high fractions of carbon monoxide, carbon dioxide, nitrogen and a small fraction of hydrogen. Just like TG, BFG contains H_2, although in a lower fraction. A final potential source, containing up to 50 mol% of carbon species is biogas, which is produced in the degradation process of biomass using bacteria. The biogas stream consists of CO_2 and CH_4, both at high partial pressure, with typically 25-50 mol% CO_2 and 50-75 mol% CH_4 [63]. Compositions of the TG, BFG and biogas are given in Table 1.2.

Direct air capture

A final option for CCU can make use of the capture of CO_2 from air. Compared to the other two capture options (post-combustion and high partial pressure sources) air contains the lowest CO_2 fraction, with only

400 ppm or 0.04% [11]. To capture the CO_2 from air, fans are used to blow air on a solvent in an absorption column. By using heat the CO_2 is regenerated and released at high purity [17]. Due to the low concentration of CO_2 this is a relatively expensive carbon capture option compared to other capture methods [38].

1.4. Water and CO_2 electrolysis

Through hydrogenation reactions different kind of products can be synthesized from CO_2. Therefore, addition of hydrogen is required as feedstock. Renewable hydrogen can be obtained by means of water electrolysis using proton exchange membrane (PEM) or solid oxide electrolysis cell (SOEC). Besides water electrolysis, different electrolysis routes exist, such as CO_2 electrolysis or co-electrolysis. Through combination of the electrolysis technologies different compositions of syngas can be produced.

1.4.1. Electrolysis principles

One of relevant factors used in electrolysis is the theoretical operating voltage, which can be calculated from the Gibbs free energy. The Gibbs free energy is important in electrolysis technology. It is defined as the minimum work required to drive the reaction. In electrolysis reactions, Gibbs free energy is dependent on the temperature and decreases as temperature increases. As a result higher temperatures yield a lower theoretical required voltage to operate the electrolysis cell. However, the total energy required for reaction is based on the Gibbs free energy and the required heat, according to Eq. 1.3, with H and G the enthalpy and Gibbs free energy changes of reaction respectively, T temperature in K and S entropy change [18].

$$\Delta H = \Delta G + T\Delta S \tag{1.3}$$

The total energy demand for the reaction, ΔH for water electrolysis with respect to the temperature, can be found in Figure 1.4. As can be seen from Figure 1.4, the electrical energy demand decreases with increasing temperature, but the heat demand increases with approximately the same amount, resulting in a total energy demand that only increases slightly with respect to increasing temperature.

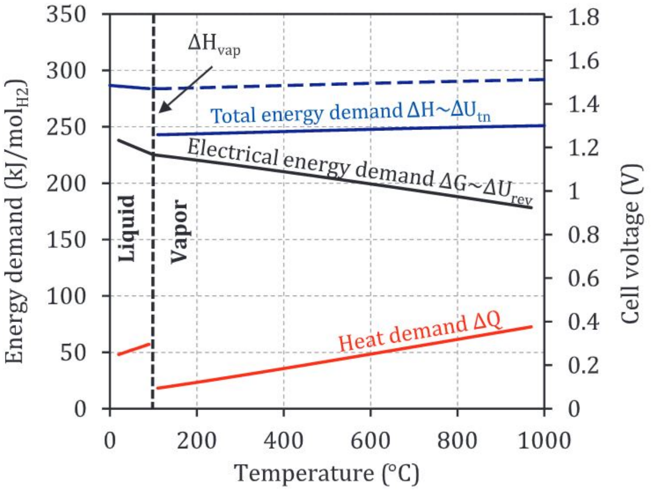

Figure 1.4: ΔG, ΔH and TΔS (ΔU) for different temperatures versus cell voltage in case of water electrolysis [12]

As mentioned, the theoretical cell voltage is based on the Gibbs free energy and thus decreases with increasing temperature, whereas thermoneutral voltage which is based on the total energy demand, remains relatively constant while operating above 100°C. The thermoneutral voltage represents the minimum voltage at which the cell produces enough heat and electrical power to operate. The equation for the thermoneutral cell voltage (V_{tn}) is shown in Eq. 1.4, where n is the number of electrons required for the reactions and F the Faradays constant [42].

$$V_{tn} = \frac{\Delta H}{nF} \tag{1.4}$$

1.4.2. PEM electrolysis

Proton exchange membrane (PEM) electrolysis is used to produce hydrogen, through electrolysis of water. Using PEM water electrolysis water is split at the anode side in hydrogen ions and oxygen. The hydrogen ions pass through the membrane, react at the cathode and form hydrogen gas. At 298K and 1 atm the theoretical voltage required for electrolysis is 1.23V based on the Gibbs free energy. Typical operating temperatures for PEM electrolysis are 60-90 °C [12]. Anodic, cathodic and overall reactions are shown in Eq. 1.5-1.7 [42].

$$\text{Anode:} \quad H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \tag{1.5}$$

$$\text{Cathode:} \quad 2H^+ + 2e^- \longrightarrow H_2 \tag{1.6}$$

$$\text{Overall:} \quad H_2O \longrightarrow \frac{1}{2}O_2 + H_2 \tag{1.7}$$

1.4.3. SOEC electrolysis

Compared to PEM, SOEC is operated at relatively high temperatures between 600°C and 900°C [18]. Another difference is that SOEC has three different electrolysis options. These options are water electrolysis, CO_2 electrolysis and co-electrolysis, whereas PEM can only be operated for water electrolysis. For each electrolysis option for SOEC the anode reaction is the same, but cathode reactions vary. At the cathode side water or CO_2 (depending on the electrolysis technology) is split in to hydrogen or CO, respectively, and oxygen ions. The oxygen ions are transferred through a solid electrolyte and react to form oxygen at the anode. Due to high temperature operation SOEC is typically operated at thermoneutral voltage at which the internal heat produced by irreversibilities is consumed by the heat demand for the electrolysis reaction [12]. Another benefit of high temperature electrolysis is the capability for heat integration. However, full heat integration is never possible so preheating will be a requirement to heat up the inlet stream. For each electrolysis option, anode, cathode and overall reactions are given in Eqs. 1.8 - 1.16

Water electrolysis

Anode, cathode and overall reactions for SOEC water electrolysis are given in Eq. 1.8-1.10. The overall reaction is the same as for PEM water electrolysis, but different cathode and anode reactions occur due to different ion exchange mechanisms.

$$\text{Anode:} \quad O^{2-} \longrightarrow \frac{1}{2}O_2 + 2e^- \tag{1.8}$$

$$\text{Cathode:} \quad H_2O + 2e^- \longrightarrow H_2 + O^{2-} \tag{1.9}$$

$$\text{Overall:} \quad H_2O \longrightarrow \frac{1}{2}O_2 + H_2 \tag{1.10}$$

CO_2 electrolysis

CO_2 electrolysis using a SOEC is a relatively new technology. The anode, cathode and overall reactions for SOEC CO_2 electrolysis are given in Eqs. 1.11-1.13. CO_2 electrolysis is available on a 340 kW scale producing 1 Nm^3 of CO per 1 Nm^3 of CO_2, including purification and recycle [35, 58].

$$\text{Anode:} \quad O^{2-} \longrightarrow \frac{1}{2}O_2 + 2e^- \tag{1.11}$$

$$\text{Cathode:} \quad CO_2 + 2e^- \longrightarrow CO + O^{2-} \tag{1.12}$$

$$\text{Overall:} \quad CO_2 \longrightarrow \frac{1}{2}O_2 + CO \tag{1.13}$$

Co-electrolysis

Co-electrolysis is a combination of CO_2 electrolysis and water electrolysis in which both reactions occur simultaneously at the cathode as can be seen in Eq. 1.15. One of the requirements for co-electrolysis is the presence of a minimum of 10 mol% of H_2 at the cathode to prevent oxidation of the catalyst. This hydrogen can be supplied by recycling some of the produced hydrogen [13]. Co-electrolysis is a relatively new technology with a max scale up to 10 kW [24]. The half reactions for anode and cathode and the overall reaction are shown in Eqs. 1.14, 1.15 and 1.16.

$$\text{Anode:}\quad 2O^{2-} \longrightarrow O_2 + 4e^- \tag{1.14}$$

$$\begin{aligned} \text{Cathode:}\quad & CO_2 + 2e^- \longrightarrow CO + O^{2-} \\ & H_2O + 2e^- \longrightarrow H_2 + O^{2-} \end{aligned} \tag{1.15}$$

$$\text{Overall:}\quad CO_2 + H_2O \longrightarrow O_2 + CO + H_2 \tag{1.16}$$

1.4.4. Power consumption

To power the electrolysis reaction a certain demand needs to be supplied in terms of $kWh/kg_{product}$. This power consumption (PC) varies per electrolysis technology and product. Table 1.3 gives a summary of values as found in literature and from manufacturers.

Table 1.3: PC (power consumption) data from literature and manufacturers for the different electrolysis technologies discussed in section 1.4. PC values are given in kWh per normal cube (Nm^3) and kWh per kg product. The PC for co-electrolysis is per Nm^3/kg of SG (syngas)

PEM water electrolysis			
PC [$kWh/Nm^3, H_2$]	PC [$kWh/kg, H_2$]	specifications	ref.
4.5	50	70 bar, 55°C model & experimental	[18]
4.5-5.5	47-62	Literature data (expert elicitation)	[52]
5.0-5.4	56-60	Hydrogenics hyLyzer (commercial 1.5-25 MW)	[57]
5.4	60	Siemens Silyzer 200 (commercial, up to 5 MW, 35 bar)	[7]
4.8	53	Siemens Silyzer 300 (commercial, up to 17.5 MW, 35 bar)	[7]
3.9-4.8	44-53	2030 forecast	[8]
SOEC water electrolysis			
PC [$kWh/Nm^3, H_2$]	PC [$kWh/kg, H_2$]	specifications	ref.
3.9	44	10bar, 800°C, thermal energy not included in PC	[18]
3.5	39.2	Haldor Topsoe TSP-2 (under development)	[35]
3.8	42	150 kW, steam from waste heat, therm. energy excluded in PC	[46]
3.7	41.3	Sunfire Hylink (comm, 150 kW, therm. energy excluded in PC)	[23]
>3.2	>36	Literature data (expert elicitation)	[52]
SOEC CO_2 electrolysis			
PC [$kWh/Nm^3, CO$]	PC [kWh/kg,CO]	specifications	ref.
6.0-8.0	4.8-6.4	Haldor Topsoe eCOs (340 kW Comm., total PC, CO_2:CO=1:1)	[35, 58]
SOEC co-electrolysis			
PC [$kWh/Nm^3, SG$]	PC [kWh/kg,SG]	specifications	ref.
3.2	6.7	Electrical PC, 1 bar,800°C, $H_2/CO=2:1$,theoretical value	[21, 28]
3.95	8.3	Sunfire SynLink (10 kW tested, 80% efficiency (LHV)	[24]

Typical values for the power consumption of PEM water electrolysis range from 50-60 kWh per kg hydrogen. SOEC water electrolysis shows lower values ranging between 40-45 kWh per kg hydrogen. This can be explained by the fact SOEC is operated at higher temperatures and therefore requires lower voltages based on Gibbs free energy. Furthermore, SOEC electrolysis has a higher efficiency. However, in the PC values shown in Table 1.3 the thermal PC is excluded and will increase the total PC. Based on literature data from two manufacturers, NEL and McPhy, the electrolysis power consumption shows a reduction for increasing scale [1, 44]. This is illustrated in Figure 1.5, that represents the electrolysis power in terms of kWh per kg hydrogen as function of the scale in kW for PEM. As can be seen from Figure 1.5 for small scale (1-10 kW) the PC is more than 75 kWh per kg H_2, whereas at increased scale the PC drops to 50 kWh per kg hydrogen. The decrease in PC seems be limited at 50 kWh per kg H_2 for a system scale larger than 1000 kW.

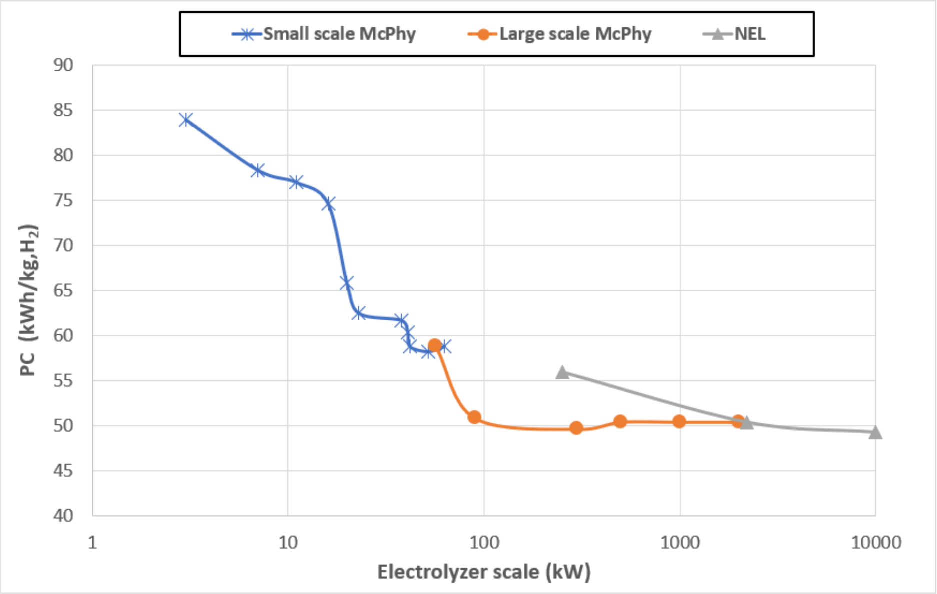

Figure 1.5: Power consumption (PC) in kWh per kg hydrogen for PEM water electrolysis with respect to the electrolyzer scale in kW based on data from two manufacturers, McPhy and NEL [1, 44].

1.5. Conversion of carbon rich syngas streams

Different syngas compositions consisting of $CO_2/CO/H_2$ can be converted to a variety of products using heterogeneous catalytic hydrogenation. Two of these options discussed in this section include methanation and methanol synthesis, which was shown in Figure 1.3. Another way to convert these syngas streams is by using GtL processes like FT synthesis. A third possible route to produce a range of products, including methanol and methane, is called electrochemical CO_2 reduction (ECR). However, at this moment ECR is only available at small scale, and will therefore be discussed briefly in Appendix A.

1.5.1. Methanation

A first potential hydrogenation product is methane. Through methanation a syngas containing CO, CO_2 and H_2 can be converted to methane. Several reactions are involved in the methanation process. These reactions are given in Eqs. 1.17 and 1.18, which represent the hydrogenation reactions for CO and CO_2 to methane, respectively. Besides both hydrogenation reactions reverse water-gas shift (RWGS) also takes place in the reactor according to Eq. 1.19.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \tag{1.17}$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \tag{1.18}$$

$$CO_2 + H_2 \longrightarrow CO + H_2O \tag{1.19}$$

Catalytic methanation has an operating range between 250-550 °C and 1-100 bar. Metals such as Ni, Ru, Rh and Co are catalyst options. However, due to a high methane selectivity, high activity and low raw material price, Ni is often considered as the catalyst of choice [27].

1.5.2. Methanol synthesis

Methanol synthesis is another hydrogenation route to convert syngas containing CO_2, CO and H_2 to methanol (CH_3OH). As was shown in Figure 1.3, the CO_2-rich stream that was separated from the TG could be upgraded by adding hydrogen from water electrolysis. The upgraded syngas is converted to methanol in a methanol synthesis reactor. The three main reactions in the methanol synthesis process include the direct hydrogenation of CO and CO_2 given in Eqs. 1.20 and 1.21, and the RWGS in Eq. 1.19 [4, 60].

$$\text{CO hydrogenation: } CO + 2H_2 \longrightarrow CH_3OH \tag{1.20}$$

$$\text{CO}_2\text{ hydrogenation: } CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \tag{1.21}$$

Both hydrogenation reactions in Eqs. 1.20 and 1.21 are exothermic. Therefore, based on Le Chatelier's principle maximum conversions are reached at lower temperatures and higher pressures [4]. In case of a $CO_2/CO/H_2$ containing syngas the reactions given in Eqs. 1.20 and 1.21 can be combined to yield Eq. 1.22.

$$a\,CO + b\,CO_2 + (2a+3b)\,H_2 \longrightarrow (a+b)\,CH_3OH + b\,H_2O \tag{1.22}$$

Depending on the catalyst, optimal operating temperature and pressure can vary. Most used commercial catalyst for CO_2 hydrogenation to methanol is Cu-ZnO-Al_2O_3 [4]. For Cu based catalysts a syngas stoichiometric ratio (SR), according to Eq. 1.23, of around 2.1 is required for optimal operation. This is slightly above SR=2, the stoichiometric condition, which means that an excess of hydrogen is supplied to the reactor. The SR is an important measure that reflects the composition that is fed to the methanol synthesis reactor, which can be seen in Eq. 1.23

$$SR = \frac{[H_2]-[CO_2]}{[CO]+[CO_2]} \tag{1.23}$$

The SR is a function of the molar compositions of reactants entering the methanol plant. When CO and CO_2 are fixed the SR only depends on the amount of hydrogen added to the reactor. By changing the hydrogen mass flow the SR can be adjusted. The optimal CO_2 concentration in the feed varies between 2.5-3.5 mol% [30].

Operating conditions

Commercial methanol plants are typically operated between 240-260 °C and 50-100 bar. However, as mentioned following from le Chatelier's principle higher pressures increase the conversion of CO_2 and at the same time increase selectivity towards methanol. When operated between 260-280° the selectivity towards methanol increased from 25% at 46 bar to 98% at 442 bar. The same effect was demonstrated for the conversion of CO_2, showing an increase from 20% to 90% for the same pressure range between 46 and 442 bars, respectively [22]. So at higher pressures both CO_2 conversion and selectivity towards methanol increase significantly.

1.5.3. Fischer-Tropsch

Another option to convert a certain $CO/CO_2/H_2$ composition could be to use GtL processes, such as Fischer-Tropsch (FT) synthesis. FT synthesis is a production route to convert syngas to a range of products with increasing C molecules. In classical FT a CO/H_2 containing syngas is fed into a reactor and converted to a range of products including: natural gas liquids (NGL: C_1 - C_4), gasoline (C_5 - C_{11}), diesel (C_{12} - C_{19}) and waxes (C_{20+}) according to Eq. 1.24 [5].

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O \tag{1.24}$$

The other pathway for FT synthesis starts with CO_2 and H_2, which has two different routes: (1) CO_2 is directly converted to FT products, (2) CO_2 is converted to CO through RWGS and the CO is converted in the classical way to products according to Eq. 1.24. However, it is believed that in the direct hydrogenation of CO_2, the RWGS reaction initially converts the CO_2 to CO, which is then converted to FT products according to Eq. 1.24 [5]. The reaction for the FT synthesis of CO_2 for different C-chains can be seen in Eq. 1.25 [47].

$$nCO_2 + (3n+1)H_2 \longrightarrow C_nH_{2n+2} + 2nH_2O \tag{1.25}$$

Catalysts that have a good activity towards FT products are Fe, Ni, Co and Ru. From those four metals only Fe and Co are feasible catalysts, because Ru is too expensive and Ni has a high selectivity towards CH_4, which is unwanted in FT [16]. Depending on the catalyst the H_2/CO ratio varies. For Co catalysts the CO/H_2 ratio is typically 2.15, while for Fe based catalysts this ratio is 1.7.

Chain-growth in Fischer-Tropsch

One the most determining factors in FT synthesis is the chain-growth of species at the catalyst site, which determines the production of higher C-chained molecules. First CO is hydrogenated to form a -CH_2- group, which acts as the monomer group in the step wise chain-growth process. At each step the adsorbed hydrocarbon can be hydrogenated to form the primary FT product or an extra monomer can be added to continue the chain growth process [16, 62]. The chain-growth probability (α) defines the likeliness of the monomer group to grow with each step. Heavier molecules are produced at higher chain growth probabilities. This growth process is schematically shown in Figure 1.6 [56]. The Anderson-Schulz-Flory (ASF) distribution is widely used in literature, which reflects the final weight fraction distribution of the FT product [47, 49]. The weight fraction W_n in the FT product distribution can be determined using Eq. 1.26, with chain-growth probability α and n the carbon atoms in the chain [19].

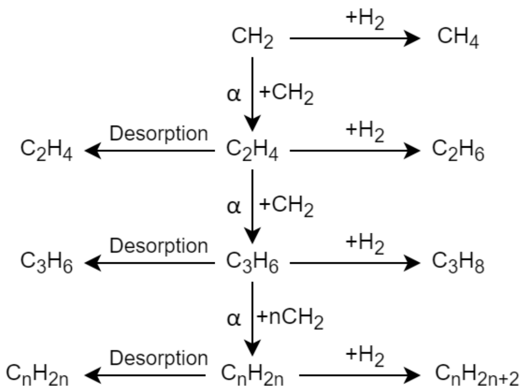

Figure 1.6: Schematic of the Chain growth during FT synthesis with α the chain-growth probability and n the number of C-atoms in the molecule [56]

$$W_n = n(1-\alpha)^2\alpha^{n-1} \tag{1.26}$$

The weight fraction distribution according to Eq. 1.26 for increasing chain growth probability α is shown in Figure 1.7 using equation. Figure 1.7 clearly shows that at higher chain growth probabilities heavier molecules are produced.

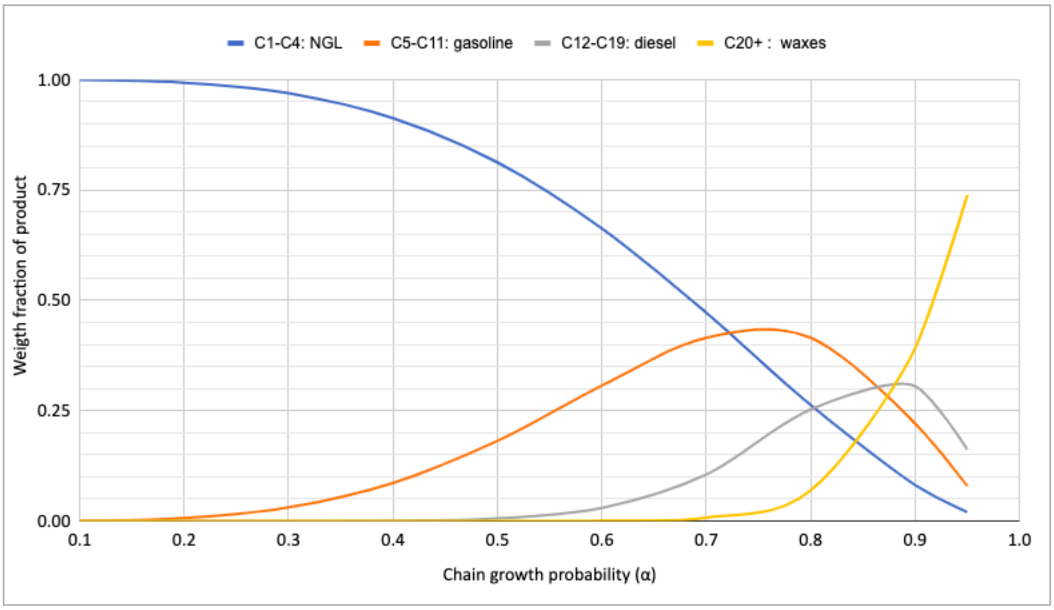

Figure 1.7: Product weight fraction distribution as a function of the chain growth probability α according to the Anderson-Schulz-Flory distribution given in Eq. 1.26 for some important product fractions: NGL (natural gas liquids), gasoline, diesel and waxes [19].

High temperature and low temperature Fischer-Tropsch

Within FT synthesis there is a difference between low temperature Fischer-Tropsch (LTFT) and high temperature Fischer-tropsch (HTFT), with respect to the product distribution. LTFT has typical operating temperatures between 180-250°C, compared to 300-350°C for HTFT [62]. At lower temperatures, α is higher leading to heavier products [33]. For an iron based catalyst the difference between LTFT and HTFT for Sasol processes is given in Table 1.4. Iron based catalyst are applicable in either LTFT or HTFT, whereas cobalt can only be used in LTFT, because production of CH_4 increases at higher temperatures [16]. What can be clearly seen from the data in Table 1.4 is the product distribution difference between high and low temperature FT. For the LTFT case almost 50 wt% of the product fraction is composed of waxes. Whereas the wax fraction in the HTFT case is only 9 wt%, and the smaller molecules fraction ($<C_{20}$) is more present in the product.

Table 1.4: Product weight fraction distribution for LTFT (low temperature Fischer-Tropsch) and HTFT (high temperature Fischer-Tropsch) for Sasol processes, using iron catalyst

Component, wt%	LTFT (220-250°C)	HTFT (330-350°C)
CH_4	4	7
C_2-C_4: Alkanes	4	6
C_2-C_4: Alkenes	4	24
C_5-C_{11}: Gasoline	18	36
C_{12}-C_{19}: Diesel	19	12
C_{20+}: Waxes	48	9
Oxygenates	3	6

1.6. Syngas generation

As mentioned in Section 1.4 renewable syngas can be generated by means of electrolysis. Different combinations of SOEC and PEM electrolysis can produce a syngas with different ratios of CO, CO_2 and H_2 [20]. Using PEM/SOEC water electrolysis in conjunction with CO_2 electrolysis, a syngas with adjustable ratios can be produced. Another possibility is co-electrolysis to directly convert water and carbon dioxide into carbon monoxide, hydrogen and oxygen. This syngas can act as feedstock for the various P2C or GtL processes discussed in Section 1.5.

Besides the renewable syngas generation route with electrolysis there is a wide range of other existing processes to generate syngas. Most conventional syngas generation routes are based on fossil fuel sources. Common production routes to generate a H_2/CO containing syngas are: SMR, partial oxidation (POX), RWGS and biomass torrefaction. These syngas generation processes can be coupled to different applications, based on the composition of the syngas. For example as discussed in section 1.5.2, methanol synthesis requires a SR of 2.

One of the non-fossil fuel syngas generation routes is SMR which was discussed in section 1.3. A syngas with a H_2/CO ratio of 3 can be produced using the SMR reaction according to Eq. 1.1. Another route to produce syngas is through the partial oxidation process of methane, as shown in Eq. 1.27. In POX, methane is mixed with sub-stoichiometric amounts of oxygen and oxidized in a burner at high temperature and pressure. This results in a syngas with a H_2/CO ratio between 1.6-2.0 [34].

$$CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2 \tag{1.27}$$

The focus in this thesis will be on the renewable syngas routes as they can be coupled to renewable energy sources.

2

Modelling of SOEC

As mentioned in Chapter 1, SOEC can be applied in different ways, whereas PEM electrolysis can only be used to produce hydrogen through water electrolysis. This chapter will elaborate further on the different electrolysis modes that exist using SOEC and in particular the amount of preheating that is required. Furthermore the effect of temperature and pressure on SOEC co-electrolysis operation will be investigated.

2.1. Modelling

SOEC water electrolysis can be used to produce hydrogen in a similar way as PEM electrolysis. The main difference is the operating temperature, since SOEC requires temperatures between 600-900 °C. A model for SOEC water electrolysis was adopted from an existing co-electrolysis model in literature by Samavati et al. (2017) and implemented in Aspen Plus [51]. The block flow diagram for the water electrolysis is schematically shown in Figure 2.1.

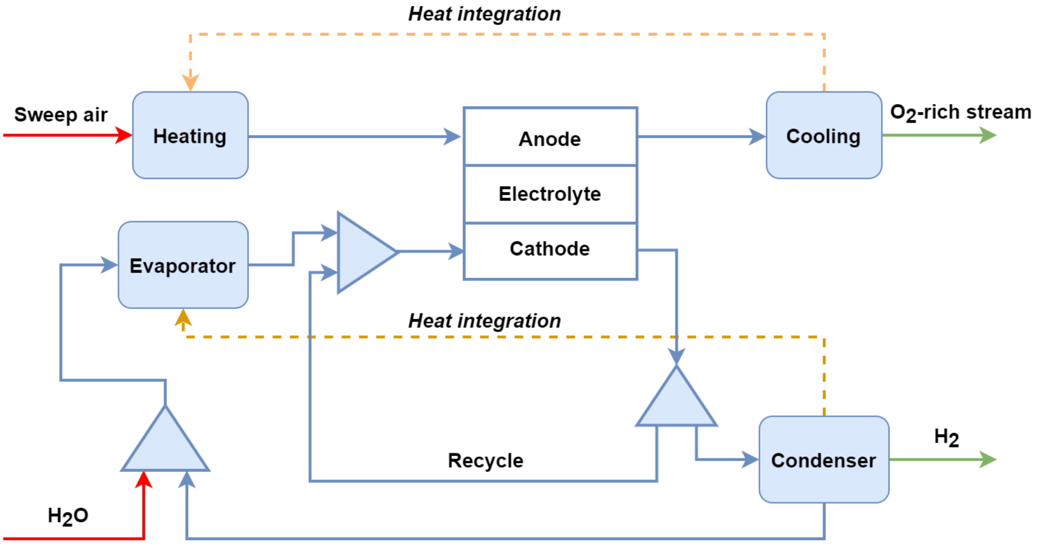

Figure 2.1: Schematic of the water electrolysis system using SOEC and possible heat integration options represented by the dashed lines. Water is mixed with the condensate from the condenser and converted to steam in the evaporator, which is mixed with the recycle stream. On the cathode side, steam is converted to hydrogen and oxygen ions, that pas through the electrolyte. The H_2-rich stream is condensed to produce H_2. Sweep air is used on the anode side to blow through the oxygen yielding a O_2-rich stream.

The orange dashed lines in Figure 2.1 represent the heat integration that is possible in the SOEC model, red lines the input of water and sweep air and green lines the output of hydrogen and oxygen-rich stream. The different steps for the SOEC water electrolysis model shown in Figure 2.1 are:

- Sweep air is used to remove oxygen produced at the anode and for thermal management purposes. The sweep air stream is heated to SOEC operating temperature and blown through the anode side to blow of the oxygen formed at anode. The sweep air mixed with the O_2, which is called the O_2-rich stream, is cooled down at the anode outlet.

- At the cathode side water is mixed with the condensate from the condenser. The water is evaporated in a steam generator. This steam is mixed with the recycle stream and converted to hydrogen, and oxygen ions that pass through the solid electrolyte. The H_2-rich stream splits into a recycle stream and a stream that is condensed to produce hydrogen.

2.2. Thermal demand and conditions

In this section the thermal demand required for the electrolysis reaction is determined using the model for SOEC water electrolysis. Besides water electrolysis SOEC has the option to operate in co-electrolysis mode. In co-electrolysis mode, CO_2 and H_2O enter the SOEC and are converted to CO an H_2, respectively. In this section temperature and pressure effects on the composition of the streams at the outlet of the SOEC are discussed for co-electrolysis operation.

Thermal demand

SOEC is operated at high temperatures. This opens up opportunities for heat integration. This can be an advantage, when integrated with waste heat. However, the high temperature operation also requires preheating, because the inlet gases can not be completely heated solely using hot outlet gases. Therefore, besides the electrical power demand, which was defined in Table 1.3, a thermal demand is necessary and should be determined. However, no literature data was found on the heat demand for SOEC electrolysis. The heat demand required for preheating is investigated using the water electrolysis model. The block flow diagram for the water electrolysis was schematically shown in Figure 2.1. This scheme was implemented in Aspen Plus and operated at thermoneutral voltage. The operating conditions are 1 bar and 850 °C. As mentioned, the dashed lines in Figure 2.1 represent the heat integration possible in the SOEC water electrolysis unit. The O_2-rich stream needs to be cooled down as it is prohibited, by environmental laws, to exhaust hot flue gasses. Besides, it is useful to utilize this heat, which would otherwise go to waste. After integration of the heat inside the SOEC model the required values for preheating can be determined. Results from the simulation yield the following values for the electrical and thermal demand, which are shown in Table 2.1.

Table 2.1: Electrical and thermal energy demands per kg hydrogen for SOEC water electrolysis and energy efficiency

Energy demands and efficiency for SOEC water electrolysis			
parameter	value	unit	description
Specific El. consumption	34.36	kWh/kg_{H_2}	electrical energy consumption per kg H_2
Specific Th. consumption	7.37	kWh/kg_{H_2}	thermal energy consumption per kg H_2
Energy efficiency	80	%	energetic energy efficiency SOEC

Judging from Table 2.1 the thermal heat required for preheating is 7.4 kWh per kg of hydrogen. For simplicity this value for the preheating is assumed to be 8 kWh per kg hydrogen. The specific electrical consumption shown in Table 2.1 is low compared to the data given in Table 1.3. One of the explanations is that the overall system efficiency is not taken into account in the SOEC model. Therefore, the electrical power consumption for SOEC water electrolysis should be higher than the simulated result shown in Table 2.1. To consider the system efficiency, an electrical PC of 42 kWh per kg hydrogen is used, based on the data given by manufacturers in Table 1.3. The thermal power consumption for the other electrolysis technologies will be based on the same fraction of heat required for the SOEC water electrolysis. In this case this is equal to 19 % of the electrical demand. The results for heat and electrical power consumption are summarized in Table 2.2. For the co-electrolysis case the composition for the outlet is based on the requirement that the SR is fixed at 2.

Table 2.2: Electrical and thermal PC (power consumption) for water, CO_2 and co-electrolysis in kWh per kg hydrogen, CO and syngas respectively using SOEC electrolysis

Thermal and electrical power consumption water electrolysis			
parameter	value	unit	description
Specific el. consumption	42	kWh/kg_{H_2}	electrical PC per kg H_2
Specific th. consumption	8	kWh/kg_{H_2}	thermal energy consumption per kg H_2
Thermal and electrical power consumption CO_2 electrolysis			
parameter	value	unit	description
Specific el. consumption	5.0	kWh/kg_{CO}	electrical PC per kg CO
Specific th. consumption	1.0	kWh/kg_{CO}	thermal PC per kg CO
Thermal and electrical power consumption co-electrolysis			
parameter	value	unit	description
Specific el. consumption	7.2	kWh/kg_{syngas}	electrical PC per kg syngas (9:3:1, H_2,CO,CO_2)
Specific th. consumption	1.4	kWh/kg_{syngas}	thermal PC per kg syngas (9:3:1, H_2,CO,CO_2)

As can be seen from Table 2.2 for SOEC water electrolysis, 42 kWh electrical and 8 kWh thermal energy is required to produce one kg of hydrogen. This gives a resulting 50 kWh total energy requirement for the production of one kg of hydrogen. Therefore, SOEC requires less energy than PEM electrolysis, which had a PC of 55 kWh per kg H_2 on average.

Pressure

The effect of co-electrolysis operated at fixed temperature and varying pressure is presented in Figure 2.2. The pressure is varied between 1 and 25 bar while temperature is fixed at 800 °C. As can be seen from the figure increased pressures result in a linear increase in amount of methane produced. At 25 bar the methane content in the outlet of the SOEC increases up to 14 mol%. Therefore, when operating the SOEC, the pressure needs to be kept at 1 bar to prevent the methanation reaction from taking place. At every pressure point the stoichiometric ratio is fixed at 2 to make sure the output is suitable to use in the conversion reactions.

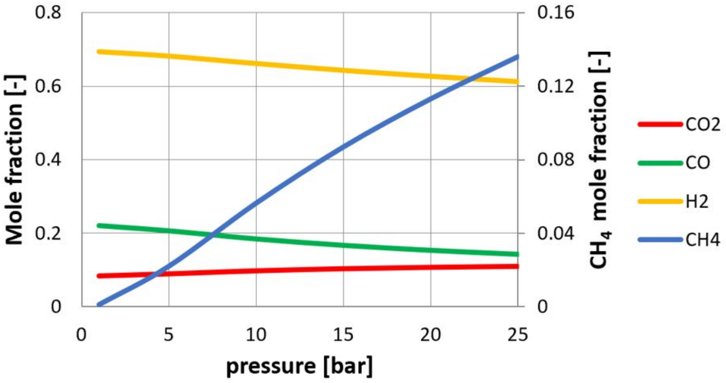

Figure 2.2: SOEC co-electrolysis pressure effect versus compositions in mole fraction of CO_2, CO, H_2 and CH_4 at 800 °C. CO_2, CO and H_2 mole fractions are given on the left axis while CH_4 mole fraction is given on the right axis. Mole fractions of the CO_2, CO, H_2 and CH_4 add up to one for each pressure point.

Temperature

A similar graph can be plotted for variations in temperature. In this case the pressure is fixed at 1 bar, to make sure no methane is formed as a result of the influence of pressure. The temperature is varied between 750-850 °C. The result is shown in Figure 2.3. It shows that fluctuations of the temperature have almost no effect on the formation of methane. Based on Figure 2.3 and Figure 2.2 the effect on outlet composition, with respect to the methane produced, is much more significant in case of pressure variations compared to temperature variations. However, temperature variation has minor effect on the composition of the other species, CO_2, CO and H_2. The CO/CO_2 ratio in the SOEC increases with increasing temperature up to 3 at 850 °C.

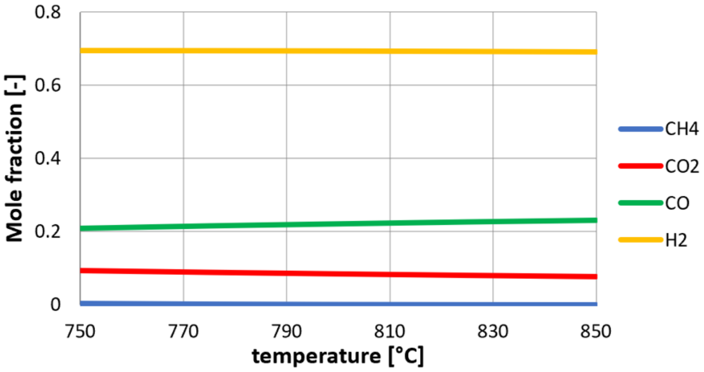

Figure 2.3: SOEC co-electrolysis as function of temperature at fixed pressure of 1 bar, for the composition in mole fraction of CO_2, CO, H_2 and CH_4

3

Pathways for CCU

Gas streams that contain high amounts of carbon species are beneficial for CCU pathways. As high amounts of CO_2 and CO lower the capture costs. Another aspect of these streams that would benefit CCU is the presence of hydrogen, since less hydrogen has to be added in the conversion step. This chapter will focus on the three main carbon rich streams, mentioned in Section 1.3: TG, BFG and biogas. SOEC and PEM electrolysis are used as a link between CO_2-rich syngas and possible products. By using electrolysis the syngas can be adjusted to the desired ratio of carbon species/hydrogen to assure a SR of 2.

3.1. Capture routes

Three gas streams, tail-gas, blast furnace gas and biogas, mentioned in Chapter 1, are discussed in this section together with the specific pathways for CCU. Different cases will be defined based on the difference in CO/CO_2 ratios in the gas streams.

Tail-gas from SMR

CO_2 removal An interesting CO_2 capture option is from the tail-gas (TG) stream that is present in the SMR process, which is traditionally used to produce H_2. In this process methane is reformed and converted to a mixture of CO, H_2, CO_2 and inerts. The next step in the process is WGS to increase the production of hydrogen from CO_2 by adding steam. The WGS outlet stream is separated using PSA to produce hydrogen. The rest stream, called tail-gas, is burned in the conventional plant to generate the heat for the reforming process. The TG contains CO_2 at high partial pressure that can be captured. The composition of the tail-gas is given in Table 3.1. The CO_2 is captured from the TG, which leaves a 100% pure stream of CO_2, called the CO_2-rich stream. This CO_2-rich stream can be used in various conversion processes towards products. The remaining CO_2-lean stream still has the same heating value as a result of CO_2 having a lower heating value (LHV) equal to 0 MJ/kg and thus can still function as fuel gas. The composition of the CO_2-rich and lean streams are given under the red columns in Table 3.1.

CH_4 removal Another option could be to remove part of the CH_4 present in the tail-gas. This is considered as a theoretical option, as CH_4 removal is much more difficult than CO_2 removal. The CO_2-lean stream is composed of only CH_4 in this case. Assumed is that 90 % of the methane can be removed from the TG, leaving a small fraction of the inert CH_4 in the CO_2-rich stream. Both CO_2-lean and rich streams can be seen in Table 3.1 under the columns marked in green. The CO_2-lean stream lacks thermal energy and requires addition of methane to increase the LHV of the stream. Adding methane will assure that enough heat can be supplied for the WGS/SMR processes.
A schematic representation for both options is given in Figure 3.1. The line in red represents the capture of CO_2 from the tail-gas and in green when CH_4 is removed. In both options the removal rate is taken as 90% of the mole fraction.

Table 3.1: CO_2-lean and CO_2-rich streams in case adjustments are made to the conventional TG (tail-gas) from steam methane reforming, when removing CO_2 or CH_4.

Compound	TG composition [mol%]	CO_2-rich [mol%]	CO_2-lean [mol%]	CO_2-rich [mol%]	CO_2-lean [mol%]
CO_2	43.0	100.0	7.0	50.2	0
H_2	28.0	0.0	45.7	32.7	0.0
CO	10.5	0.0	17.1	12.3	0.0
N_2	2.5	0.0	4.1	2.9	0.0
CH_4	16.0	0.0	26.1	1.9	100.0

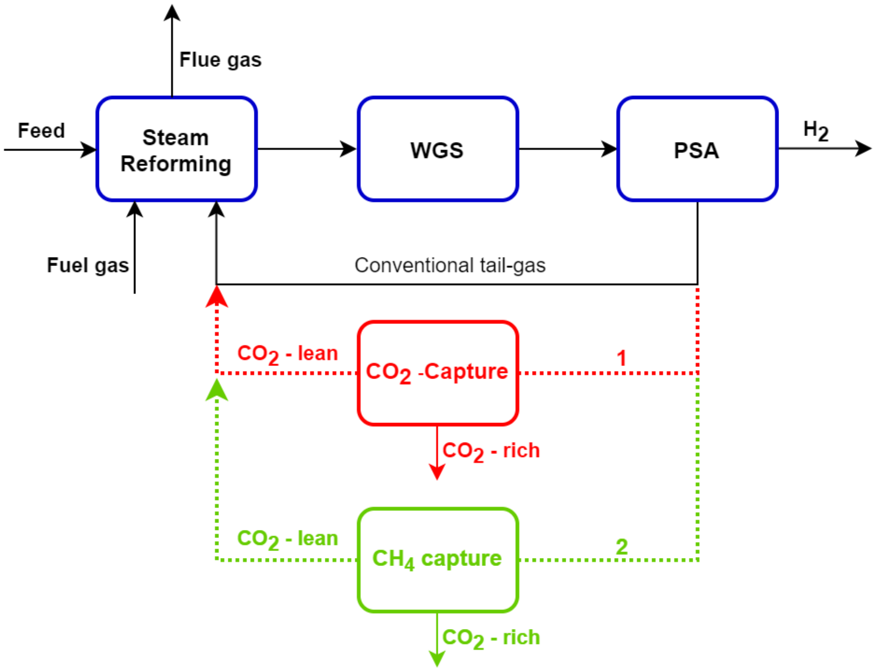

Figure 3.1: Adaptation of the conventional steam methane reforming process to produce hydrogen, with steam reforming, WGS (water-gas shift) and PSA (pressure swing adsorption). The line in red represents CO_2 removed from the tail-gas and the line in green when methane is removed. The green route is considered as a theoretical case.

Blast furnace gas

Blast furnace gas (BFG) is produced in the steel manufacturing process and consists of H_2, CO_2, CO and N_2. Typical molar compositions for blast furnace gas are 5-10 mol% H_2, 20-25 mol% CO, 20-25 mol% CO_2 and the largest fraction 40-45 mol% N_2 [26]. This gas can be used to generate electricity or steam, and is typically used in the steel industry as an addition to methane.

N_2 removal A first option is to remove part of the nitrogen from the BFG. This is also a theoretical option similar to CH_4 removal as N_2 cannot be selectively removed from other gases in the stream. As mentioned before the BFG contains high concentrations of CO_2, CO and some hydrogen, which makes the stream useful in CCU processes. Assumed is that 5 mol% of the nitrogen remains in the CO_2-rich stream, which equals a 92.1% removal rate of the nitrogen. The compositions for the CO_2-rich and lean stream are given in the columns marked in purple.

CO_2 removal The other route for CCU could be to remove the CO_2 from the BFG at 90% removal rate. This stream is called the CO_2-rich stream. This route is similar to CO_2 removal from the TG, in which the CO_2-lean stream can be used to burn and generate heat that is integrated in the steel manufacturing process. For both BFG options the CO_2-rich and CO_2-lean streams are given in Table 3.2 marked under the blue columns.

Table 3.2: CO_2-lean and CO_2-rich stream compositions in mol% in case adjustments are made on the conventional BFG, when removing N_2 or CO_2

Compound	BFG composition [mol%]	**CO_2-rich [mol%]**	**CO_2-lean [mol%]**	**CO_2-rich [mol%]**	**CO_2-lean [mol%]**
CO_2	25.0	39.6	0.0	100.0	2.4
H_2	10.0	15.8	0.0	0.0	12.2
CO	25.0	39.6	0.0	0.0	24.4
N_2	40.0	5.0	100.0	0.0	61.0
CH_4	0.0	0.0	0.0	0.0	0.0

Biogas

Biogas is produced by the bacterial degradation of biomass in biogas plants. It contains high concentrations of carbon dioxide and methane, between 25-50 mol% and 50-75 mol%, respectively. Therefore, it can be considered as another high partial pressure source of CO_2. Besides CO_2 and CH_4 it contains 2-8 mol% of other gases, such as hydrogen, oxygen and nitrogen. To get rid of pollution in the biogas, the gas is desulphurized and treated, which leaves a high purity stream of CO_2 and CH_4 [63]. This gas is typically used to generate heat. As a result of the high concentration of CO_2, the biogas has significant application in CCU processes. All the cases with corresponding compositions of the carbon-rich streams are presented in Table 3.3, distinguished on CO/CO_2 basis ranging between 0-4. These carbon rich streams can be be upgraded by making use of PEM or SOEC electrolysis.

3.2. Upgrading of the syngas

The gas streams from the previous section need to be upgraded to acquire the correct carbon/hydrogen ratio, such that the SR for each case is fixed at 2. Electrolysis using SOEC and PEM technology will be used to supply hydrogen or in some cases to adjust the CO/CO_2 ratio. For the streams containing only CO_2, CO_2-electrolysis or co-electrolysis are options to produce CO, which is both required for FT synthesis and desired for methanol synthesis. Each case will be distinguished by the respective CO/CO_2 ratios in the syngas, ranging from 0-4. A schematic of each case is given in Figure 3.2. Each case will be discussed in more detail below.

Table 3.3: Raw syngas and upgraded syngas composition after electrolysis for each Case in mol% and the CO/CO_2 ratio afiliated with the cases

Raw gas composition in mol%							
Case	Gas stream	CO_2	CO	H_2	N_2	CH_4	CO/CO_2
1	TG, BFG or biogas	100	0.0	0.0	0.0	0.0	0.0
2	TG, BFG or biogas	7.7	23.0	69.0	0.0	0.0	3
3	TG, BFG or biogas	20.0	80.0	0.0	0.0	0.0	4
4	TG	50.2	12.3	32.7	2.9	1.9	0.25
5	BFG	39.6	39.6	15.8	5.0	0.0	1
Upgraded gas composition in mol%							
Case	Gas stream	CO_2	CO	H_2	N_2	CH_4	CO/CO_2
1	TG, BFG or biogas	24.9	0.0	75.1	0.0	0.0	0.0
2	TG, BFG or biogas	7.7	22.9	69.4	0.0	0.0	3
3	TG, BFG or biogas	6.2	24.9	68.8	0.0	0.0	4
4	TG	20.6	5.0	72.4	1.2	0.8	0.25
5	BFG	14.0	14.0	70.3	1.7	0.0	1

CO_2 removal from tail-gas

The CO_2 is removed from the TG, leaving a 100% pure CO_2-rich stream. This pure CO_2 can be upgraded by applying different electrolysis technologies. Three of these cases are discussed:

- **Case 1** : The CO_2-rich stream is upgraded by adding hydrogen from PEM or SOEC water electrolysis, equal to the amount required for the desired product. In this case the hydrogen addition is equal to the amount required to acquire a SR of 2. The ratio of **CO/CO_2 is 0** in this case.

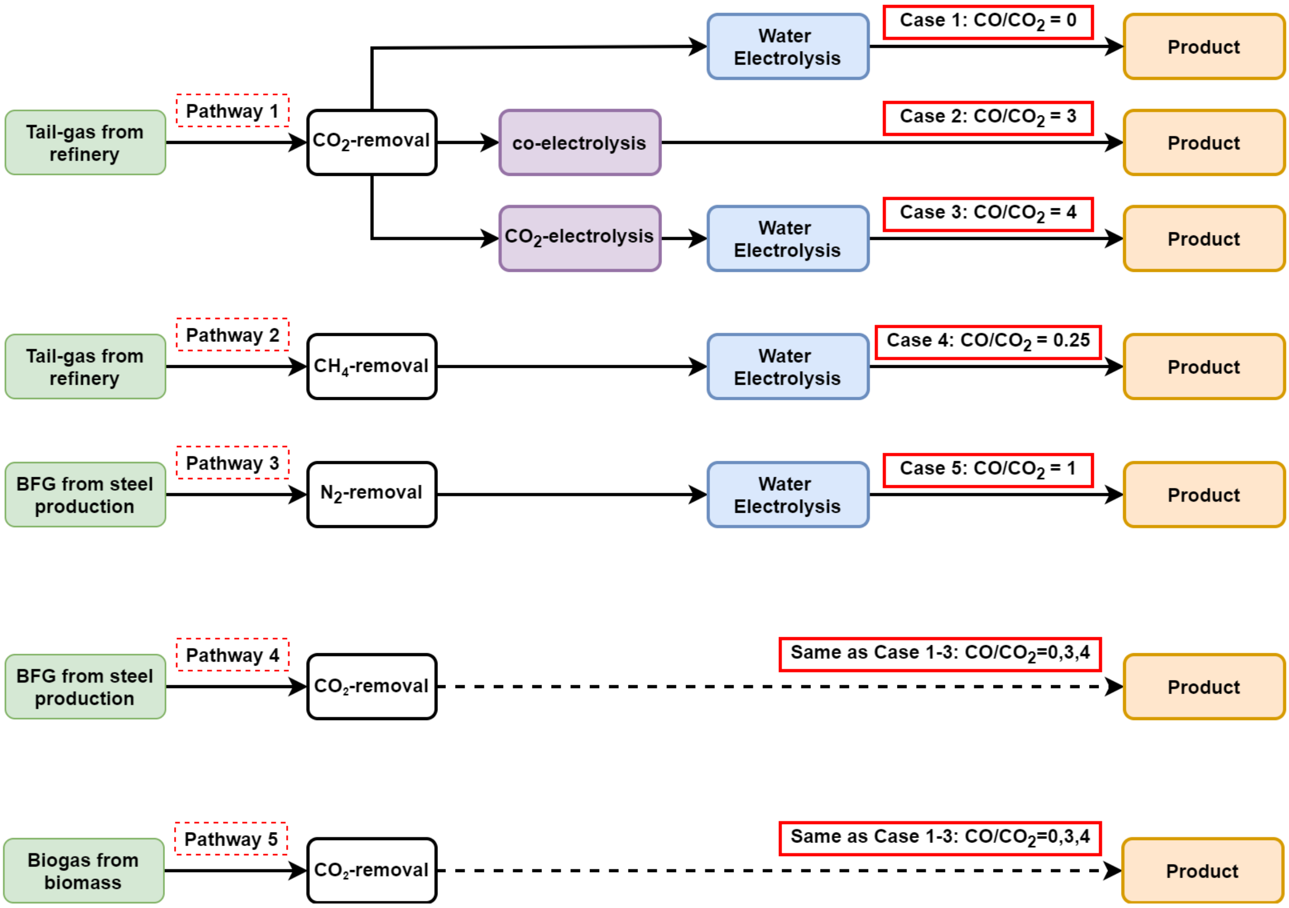

Figure 3.2: Schematic of the different capture routes with corresponding cases for the BFG, TG and biogas. The CO_2-lean streams are not depicted as they are no longer used. As mentioned before Case 4 and Case 5 represent the two theoretical cases, because CH_4 and N_2 are difficult to selectively remove from the other gasses.

- **Case 2** : The CO_2-rich stream is upgraded by applying SOEC co-electrolysis technology. The water is mixed with the CO_2 as an input to the SOEC, which converts it into a mixture of H_2, CO_2 and CO. **The CO/CO$_2$ ratio is equal to 3**, which is acquired after the co-electrolysis step. This ratio could be observed from Figure 2.3 in Chapter 2, in case the SOEC was operated at 1 bar and 850 °C.

- **Case 3** : Through another route the pure CO_2 stream can be converted to CO first using the option of SOEC CO_2-electrolysis. Assumed is that 80% of the CO_2 is converted in a single pass, which leaves a mixture with a **CO/CO$_2$ ratio of 4** . In a next step hydrogen is added by using water electrolysis.

CH_4 removal from tail-gas

Besides the removal and utilization of CO_2, methane could also be removed to acquire a CO_2-rich syngas that contains CO_2, CO, H_2 and some inerts (N_2 and CH_4)

- **Case 4**: For the second option, methane is removed from the tail-gas, leaving the CO_2-rich stream. Hydrogen is added to this stream according to the required amount for the desired product. **This syngas contains a CO/CO$_2$ ratio equal to 0.25**.

N_2 removal from BFG

The BFG has one unique case. By removing some of the inert nitrogen a gas stream is obtained that contains CO_2, CO, H_2 and some N_2.

- **Case 5**: The CO_2-rich stream that remains after the removal of N_2 is upgraded with hydrogen from water electrolysis. **This case contains a CO/CO$_2$ ratio equal to 1**.

CO_2 removal from BFG

The option for CO_2 removal from the BFG has the same possible cases as discussed for CO_2 removal from TG. The starting point is a 100% pure CO_2 stream captured from the BFG. Therefore, this option will not be discussed in further detail as it will yield the CO/CO_2 ratios equal to 0, 3 and 4.

CO_2 removal from biogas

This is again a similar option as the removal of CO_2 from either BFG or TG. The starting point is a 100% pure CO_2 stream captured from the biogas. Therefore, this option will not be discussed in further detail as it will yield the CO/CO_2 ratios equal to 0, 3 and 4. Furthermore, a summary of each case with their respective compositions after addition of the hydrogen from electrolysis is given in Table 3.3.

4

Marginal cost price analysis

In this chapter prices for the feedstock will be defined. The feedstock costs will form the link between the mass and energy balances and the costs for the products that will be discussed in Chapter 5. This link can be made through the determination of feedstock prices, such as hydrogen and CO_2, that are affected by variable costs such as electricity prices and CO_2 capture costs. By selecting variable costs, feedstock prices can be fixed, which allows the calculation of product prices. Furthermore, a selection of products is made, based on the feasibility of the marginal cost price analysis.

4.1. Methodology

The main idea of the marginal cost price analysis is to focus on the operational expenditure (OPEX). The marginal cost price is the income derived from the sales of the product subtracted by the cost of the raw material [53]. By computing the raw material cost and comparing it to the market price an initial estimate can be made on the feasibility of the production route. If the raw material cost of the product is already higher than the market price, that specific production route will not be feasible. As additional costs have to be added to acquire the total cost price. In Appendix B an example is shown based on the marginal cost price analysis of CH_4. The OPEX consists of all the costs required to run the process. This includes the prices for the feedstock and labour costs for example. In process industry feedstock is defined as the raw material required for the chemical reactions. In this thesis the term feedstock will be taken in a broader sense, where electricity, steam and hydrogen price are included. This chapter will give an overview of the cost for the relevant feedstock.

4.2. Electricity price

One of the required feedstock is the electricity price that varies from country to country and from consumer to industry, throughout the year. A range for the electricity prices is specified based on the prices reported in the quarterly reports from the European commission for the year 2018 and the first three quarters of 2019[14].

Table 4.1: Highest, lowest and average electricity prices as reported by the European Commission for the year 2018 and the first three quarters (Q1, Q2 and Q3) of 2019 in €/MWh

EU electricity prices in 2018	Lowest price	Highest price	Average price
Q1	33.9	59.6	45.3
Q2	33.9	60.1	43.8
Q3	35.5	71.3	59.7
Q4	47.1	72.2	61.7
EU electricity prices 2019	**Lowest price**	**Highest price**	**Average price**
Q1	40.8	68.0	48.9
Q2	33.4	65.5	43.3
Q3	33.6	66.3	47.0

Looking at the data in Table 4.1, prices for electricity could go as high as 72.2 €/MWh during 2018 Q4 to as low as 33.4 €/MWh in 2019 Q2.

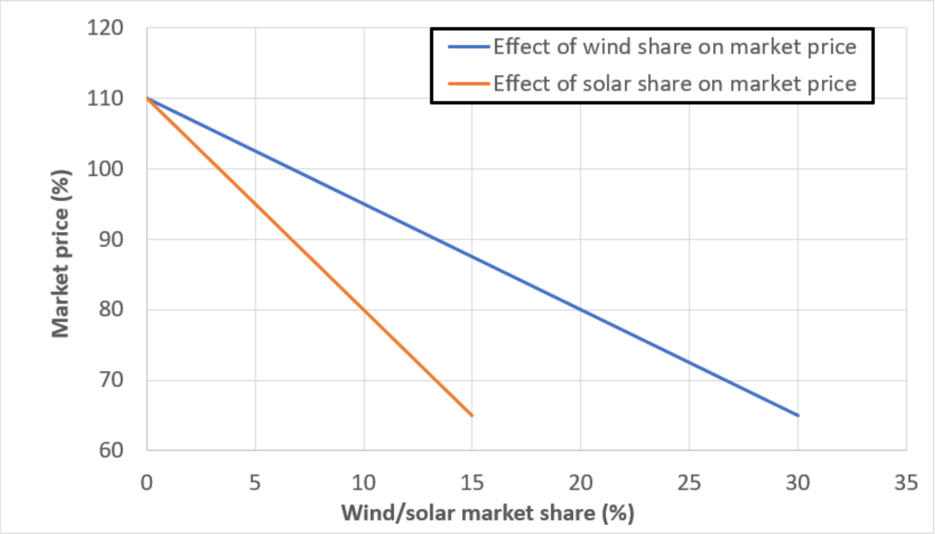

Figure 4.1: Effect of the percentage of solar/wind share as a percentage of the market price based on data from Hirth (2013) [31].

An interesting observation is that based on an increased share of renewable energy in the power supply, as a result the electricity price seems to decrease. As penetration of wind and solar power increases, the electricity market price decreases. This is demonstrated in Figure 4.1, which shows that as the share of wind and solar power increase, the market price drops as a result. For a solar share of 15 % the market price drops from 110 % to 65 %. The same decrease is observed for a wind share of 30 % [31]. This means that in a future scenario when renewable energy sources are becoming more available, electricity prices might drop below the prices given in Table 4.1. Due to the fluctuation in electricity prices, it would make sense to assess the economical feasibility, in the coming Chapter for a range of values. Therefore, an electricity price range between €20-50 per MWh is selected.

4.3. Steam price

The steam price is typically linked to the price for methane, as steam is traditionally produced using heat from burning methane. Other ways to produce steam are through renewable routes such as concentrated solar power, biogas or biomass. For these steam production routes, three types of steam exist namely, low pressure (LP), medium pressure (MP) and high pressure (HP), which have different pressures and temperatures [48]. Table 4.2 gives a summary of the different routes to produce steam and the associated costs. Depending on the route to produce the steam, prices range between 15-30 €/t or 21-41 €/MWh.

Table 4.2: LP (low pressure), MP (medium pressure) and HP (high pressure) steam prices in €/ton and €/MWh produced from natural gas (NG), concentrated solar power (solar), biomass and biogas processes [48]

Steam type	Conditions	NG		solar		biomass		biogas	
		€/t	€/MWh	€/t	€/MWh	€/t	€/MWh	€/t	€/MWh
LP	2.07 bar, 122C	15.1	21.5	29.3	41.6	18.4	26.1	24.7	35.1
MP	27.6 bar, 230 C	15.8	21.6	29.9	40.9	18.9	25.9	25.1	34.4
HP	42.5 bar 320 C	17.1	21.7	29.5	37.5	20.3	25.8	26.2	33.3

4.4. Hydrogen cost price

Some of the cases defined in Chapter 3 required addition of hydrogen for the synthesis process. Hydrogen produced in a renewable way using electrolysis, requires large amounts of electricity produced by solar, wind or hydro power. In this section for both PEM and SOEC electrolysis the price for hydrogen will be defined.

PEM

The power consumption for PEM water electrolysis is between 50-60 kWh per kg hydrogen, according to manufacturers and literature data, which was seen from Table 1.3. Therefore, in the calculation for the cost price, a PC of 55 kWh per kg hydrogen is used. There are two aspects that define the hydrogen price: the operational expenditure (OPEX) and the capital expenditure (CAPEX). Table 4.3 gives the relevant parameters needed for the calculation of the OPEX and CAPEX.

Table 4.3: Parameters required for the calculation of PEM and SOEC capital and operational expenditures (CAPEX and OPEX)

CAPEX parameters			
constant	symbol	Value	units
PEM/SOEC investment	INV_{PEM}	1000 [6]	€/kW
Operational hours per year	H	8500	h/y
Electricity price	$C_{electricity}$	40	€/MWh
Lifetime PEM/SOEC	L	20 [6, 10]	y
PEM parameters			
PEM H_2 PC	PC_{PEM}	55	kWh/kg
SOEC parameters			
SOEC H_2 PC	PC_{SOEC}	42	kWh/kg
SOEC H_2 thermal demand	TH_{SOEC}	8	kWh/kg
Steam price	C_{steam}	30	€/MWh

The CAPEX ($CAPEX_{PEM}$) for the H_2 production in euros per kg H_2 for PEM water electrolysis can be calculated using Eq. 4.1 with the data from Table 4.3.

$$CAPEX_{PEM} = \frac{INV_{PEM} \cdot PC_{PEM}}{L \cdot H} \tag{4.1}$$

The next step is to calculate the OPEX ($OPEX_{PEM}$) for the hydrogen in euros per kg H_2, using Eq. 4.2, which is the product of the electrolysis power consumption and electricity price.

$$OPEX_{PEM} = PC_{PEM} \cdot C_{electricity} \tag{4.2}$$

With the parameters defined in Table 4.3 a CAPEX of € 0.32 and OPEX of € 2.20 can be calculated, which yields a total price of € 2.52 per kg of hydrogen. In industry CAPEX is often estimated as a function of the OPEX. A CAPEX of € 0.32 and OPEX of € 2.20 result in a CAPEX/OPEX ratio of 0.15. However, the CAPEX/OPEX ratio is solely dependent on the electricity price, as the OPEX is a function of the electricity price. In this case the CAPEX is fixed and irrespective of the electricity price. For three electricity prices of €30, €40 and €50 per MWh the OPEX, CAPEX and CAPEX/OPEX ratios are given in Table 4.4.

Table 4.4: OPEX, CAPEX and CAPEX/OPEX ratio of PEM water electrolysis at different electricity prices

Electricity price €/MWh	OPEX €/kg,H_2	CAPEX €/kg,H_2	CAPEX/OPEX [-]
30	1.65	0.32	0.20
40	2.20	0.32	0.15
50	2.75	0.32	0.12

As can be seen from Table 4.4 the CAPEX/OPEX ranges from 0.12 for 50 €/MWh to 0.20 for 30 €/MWh. A typical value used for the CAPEX/OPEX ratio in the chemical process industry is 0.20 [15]. Therefore, in the coming sections a ratio for the CAPEX/OPEX of 0.20 will be assumed to take into account all equipment costs, which is in the same order of magnitude as the values calculated in Table 4.4.

SOEC

The calculation for SOEC is for the most part identical to PEM. The difference is the extra required costs for the heat. For the electrical power consumption 42 kWh per kg hydrogen is assumed based on literature data found in Table 1.3. The thermal demand was defined in Chapter 2 to be 8 kWh per kg H_2. Thermal and electrical energy consumption for SOEC are given in Table 4.3. The CAPEX for SOEC water electrolysis is assumed to be equal to the CAPEX for PEM water electrolysis. Therefore, the same values for investments, lifetime and operational hours per years as defined for PEM in Table 4.3 are assumed for SOEC. The OPEX ($OPEX_{SOEC}$) for hydrogen production using SOEC can be calculated with Eq. 4.3.

$$OPEX_{SOEC} = PC_{SOEC} \cdot C_{electricity} + TH_{SOEC} \cdot C_{steam} \tag{4.3}$$

Using an electricity price of €40 per MWh and steam price of €30 per ton the OPEX for SOEC water electrolysis is determined at € 1.92 per kg H_2. The CAPEX is € 0.32 per kg H_2 which was assumed to be equal to the PEM water electrolysis CAPEX. This yields a total hydrogen cost price of € 2.24 per kg of hydrogen, which is lower compared to PEM water electrolysis.

4.5. CO_2 capture price

The price for carbon dioxide mainly depends on the source from which it is captured. As discussed in Section 1.3, three sources were taken in to account: CO_2 from flue gas, capture from streams containing high partial pressures of CO_2 and CO_2 directly captured from air. These sources require different capture technologies and contain different amounts of CO_2, and therefore prices of the CO_2 may vary.

Flue gas

As discussed in Section 1.3, CO_2capture from flue gas is a post-combustion capture method. The CO_2 content varies from 10-15 wt%. A common applied capture technology is amine absorption. Energy requirements shown in Table 1.1 varied between 2.1-3.6 GJ per ton of captured CO_2. This energy represents the thermal requirement for the regeneration of the amines and simultaneous release of CO_2. This heat can be provided by supplying between 0.8-1.5 tons of steam [54]. Steam prices also have some variation, depending on how it is produced. Prices range from 16 €/t for natural gas based steam to 30 €/t for solar based steam as was discussed in Section 4.3. Besides thermal heat a small amount of electrical energy is demanded for compression in the process, which accounts to around 0.05 MWh per ton of CO_2 [6, 59]. For an electricity price of €40 per MWh the theoretical cost for CO_2 capture from flue gas will be in the range of €15-50 per ton of CO_2. However, this price will be higher in reality.

SMR tail-gas

Capturing CO_2 from the tail-gas produced in the SMR process, has a high CO_2 fraction between 40-45 mol%. Pressure swing adsorption (PSA) is often used to capture around 60% of the CO_2 [54]. In the traditional process the complete tail-gas without separation is burned to create heat for the steam reforming process. CO_2 capture costs from tail-gas vary between €36-72 per ton of CO_2 [54].

Direct air capture

Capturing CO_2 from air using direct air capture (DAC) is the most expensive capture technology. This is linked with the low partial pressure of CO_2 in air of only 400 ppm (0.04 %). Therefore, energy requirements are higher compared to the other sources. Around 250 $kWh_{electrical}$ and 1750 $kWh_{thermal}$ energy are required to capture 1 ton of CO_2 [17]. To supply enough thermal heat for the CO_2 capture around 2.5 tons of steam is required. With a steam price ranging between 16-30 €/t and electricity price of €40 per MWh, capture costs vary between €50-85 per ton of CO_2. This is the theoretical based cost price for CO_2 using DAC. However, based on literature data from a pilot plant, capture costs are higher in reality, ranging from 94-232 $\$/t_{CO_2}$ (86-208 $€/t_{CO_2}$) [38].

Table 4.5 shows the capture sources discussed in this section and the respective capture technology, CO_2 fraction, capture rate and capture costs per ton of CO_2. Overall flue gas has the cheapest CO_2 capture costs. However, capture from the SMR TG is in the same order of magnitude and has a higher CO_2 fraction. DAC is by far the most expensive option for acquiring CO_2.

Table 4.5: CO_2 capture represented for capture from flue gas, steam methane reforming (SMR) tail-gas and air, with corresponding capture method, CO_2 fraction, capture rate and price per ton.

Source	Capture technology	CO_2 fraction	capture rate	Price per ton of CO_2
Flue gas	absorption	10-15 wt%	90	€15-50
SMR tail-gas	PSA	40-45 mol%	60	€36-72
Air	DAC	0.04 wt%	>99%	€86-208

4.6. Economic evaluation of hydrogenation products

To select which products are the most feasible in terms of economics a comparison is made between market price and marginal cost price of hydrogenation products given in Table 4.6. A simple marginal cost price analysis can be performed to assess which products are economically feasible using hydrogenation. The cost of the product is determined by the costs required for the feedstock. In this case the cost for the products is based on the hydrogen produced by electrolysis and the capture costs of CO_2. The hydrogenation reaction, required amounts of CO_2 and H_2 to produce one ton of product for a selection of products are given in Table 4.6.

Table 4.6: Overall reaction of some potential hydrogenation products and the required amounts of CO_2 and H_2 to produce 1 ton of product

product	overall reaction	CO_2 requirement [$t/t_{product}$]	H_2 requirement [$t/t_{product}$]
Carbon monoxide (CO)	$CO_2 + H_2 \longrightarrow CO + H_2O$	1.571	0.071
Methanol (CH_3OH)	$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$	1.375	0.188
Methane (CH_4)	$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$	2.750	0.500
Ethylene (C_2H_4)	$2CO_2 + 6H_2 \longrightarrow C_2H_4 + 4H_2O$	3.143	0.429

Table 4.7: Cost shares for the CO_2 and H_2 based on the production of 1 ton of product through hydrogenation and the total product price in euros

product	CO_2 cost [€/$t_{product}$]	H_2 cost [€/$t_{product}$]	product price [€/$t_{product}$]
Carbon monoxide (CO)	79	156	235
Methanol (CH_3OH)	69	414	482
Methane (CH_4)	138	1100	1238
Ethylene (C_2H_4)	157	944	1101

Table 4.7 shows the costs for the CO_2 and H_2 required for the products as well as the total prices per ton of product. The marginal product price is calculated by summing up the H_2 and CO_2 cost shares. The main conclusion that can be drawn from Table 4.7 is that the hydrogen cost, and thus the electricity price, is the determining factor in the total price of the products. This is especially relevant for the products that require more hydrogen to produce one ton of product such as methane and ethylene. Cost prices are calculated for the hydrogenation products, to assess what the cheapest production route for certain C1 products and ethylene are compared to conventional market prices. Product costs are based on a €40 per MWh electricity price and a CO_2 price of €50 per ton.

Table 4.8: Comparison between the hydrogenation product price and the market price and size for a selection of products

product	Hydrogenation product price [€/$t_{product}$]	Market price [€/$t_{product}$]	Market size[39] [Mton]
Carbon monoxide	235	340-360[37]	>220 (syngas)
Methanol	482	350-400 [39]	110
Methane	1238	85-105[40]	200
Ethylene	1101	1000-1050[39]	140

Judging from Table 4.8 carbon monoxide has a lower cost price than the respective market price. Furthermore, CO has a big market size as it is almost always obtained in the form of syngas, through production route such as SMR. Taking in to account that the product prices for methanol and ethylene are close to the market prices, methanol and ethylene could prove to be feasible production routes. Especially when electricity and CO_2 are accessible at low prices. Going forward, methanol and FT products will be discussed in more detail in the next chapter. A big advantage of methanol and FT products is that they can be stored as liquids at room temperature, whereas ethylene is a gas. Methane appears to be the least favourable product. In Appendix B some further calculations are conducted for different cases, which demonstrate that methane will not be a feasible product.

5

Economic analysis

This chapter will discuss economic feasibility of two products: Methanol and Fischer-Tropsch liquids. The methanol cost price will be calculated using two different scenarios: Water electrolysis using PEM or SOEC. Furthermore, the effect of selling the produced oxygen and the effect of the CO/CO_2 ratio on the methanol cost price will be assessed. The cost price for the FT products will be conducted based on a gross profit analysis, which means cost prices will be calculated by solely considering the feedstock costs. Furthermore, the effect of the CO_2 and electricity price on the FT product price will be addressed.

5.1. Methanol synthesis model

In Chapter 3, five cases were defined based on the gas compositions after capture from carbon-rich gas streams, such as TG, BFG and biogas. These cases were distinguished based on the CO/CO_2 ratio, varying between 0-4. The syngas streams were upgraded by adding hydrogen produced by water electrolysis. This upgraded syngas can then be converted to different products. One of the possible products discussed in Section 1.5.2 is methanol. For the separate cases the corresponding cost price of the methanol will be analyzed. Each case will contain a different combination of CO_2, CO and H_2 compositions for the syngas entering the methanol reactor, but a SR of 2 will be fixed. The SR was defined in Eq. 1.23 as, $(H_2 - CO_2)/(CO_2 + CO)$. Because the CO_2 and CO fractions are fixed by the CO/CO_2 ratios, the amount of H_2 required is different for each case. The compositions of the syngas entering the methanol plant, after upgrading of the syngas are given in Table 5.1. For each case the compositions and amount of hydrogen that has to be added is based on the fixed SR equal to 2.

Table 5.1: Molar composition of the syngas entering the methanol reactor for each case when the SR=2 requirement is considered

Syngas compositions entering methanol reator						
Case	CO_2	CO	H_2	N_2	CH_4	CO/CO_2
1	24.9	0.0	75.1	0.0	0.0	0.0
2	7.7	22.9	69.4	0.0	0.0	3
3	6.2	24.9	68.8	0.0	0.0	4
4	20.6	5.0	72.4	1.2	0.8	0.25
5	14.0	14.0	70.3	1.7	0.0	1

Using a reference model from literature by Van Dal et.al (2013) [59], which is based on the kinetic model of Vanden Bussche and Froment (1996) [60], the methanol plant is simulated for each case using Aspen Plus. As a result from the simulation mass and energy balances are obtained. An adiabatic plug flow reactor (PFR) is used with Reactor inlet conditions of 76 bar and 483 K. The block flow diagram of the methanol plant is shown in Figure 5.1.

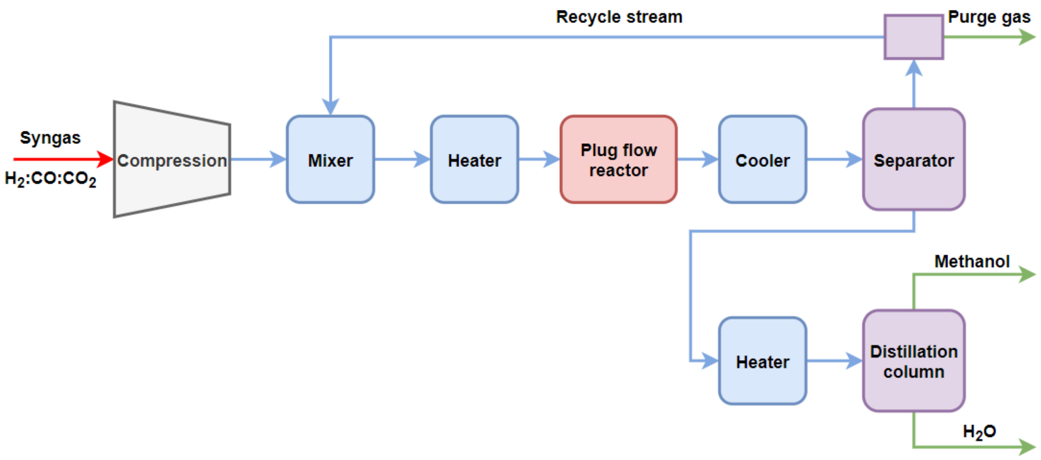

Figure 5.1: Block flow diagram of the methanol plant as proposed by Van Dal et al. [59]. In the methanol plant (1) syngas is compressed and mixed with the recycle stream, (2) this syngas is heated to the plug flow reactor (PFR) inlet temperature and converted to methanol inside the PFR. (3) The outlet stream of the PFR is cooled and separated into a recycle stream that is partially purged and a stream containing a mixture of methanol and water. (4) In the final step the methanol and water are separated inside a distillation column.

The steps in the methanol synthesis process as shown in Figure 5.1 are as follows:

1. The syngas with different compositions based on the CO/CO_2 ratio, defined in Chapter 3, is compressed and mixed with the recycle stream of the plant. The compositions of the syngas for each case are given in Table 5.1.

2. In the next step the mixed stream is heated to PFR inlet temperature and converted to methanol inside the PFR.

3. The outlet stream of the PFR is cooled. In the separator the methanol is split into a stream containing H_2O plus methanol and a recycle stream. The recycle stream is first partially purged to avoid accumulation of inert components. And then recycled and mixed with the inlet syngas.

4. In the final step the methanol and water mixture is separated in a distillation column producing methanol at high purity and water.

The methanol yield is never 100% due to the kinetics in the reactor. As a result recycling is required to improve the conversion of reactants and production of methanol. Purging is necessary when recycling to avoid accumulation of inert components and reactants. Therefore, part of the methanol reactor outlet is recycled and purge, which causes some of the feedstock (hydrogen and carbon species) to exit through the purge as well. For each case a methanol yield (Y_{CH_3OH}) can be calculated using Eq. 5.1, which is defined as the actual simulated yield (SIM_{CH_3OH}) value divided by the stoichiometric amount of methanol (ST_{CH_3OH})that could be produced from the feedstock.

$$Y_{CH_3OH} = \frac{SIM_{CH_3OH}}{ST_{CH_3OH}} \tag{5.1}$$

5.2. Methanol cost price

The model for the methanol plant is used to obtain the mass and energy balances for the different cases. The cost price of the methanol can be determined by using the feedstock prices defined in Chapter 4. This is done for a couple of scenarios: by using PEM for the hydrogen production, by using SOEC for the hydrogen production and when taking the revenues from selling the oxygen into account. Finally, the effect of the CO/CO_2 ratio will be assessed to see what effect is has on the methanol cost price.

5.2.1. Hydrogen from PEM

In the first scenario the methanol cost price will be calculated using hydrogen production from PEM water electrolysis. After simulation the mass and energy balances were obtained from the Aspen Plus model. For every case Figure 5.2 shows schematically the mass balance and thus amounts of H_2 and CO_2 required to produce 1 ton of methanol.

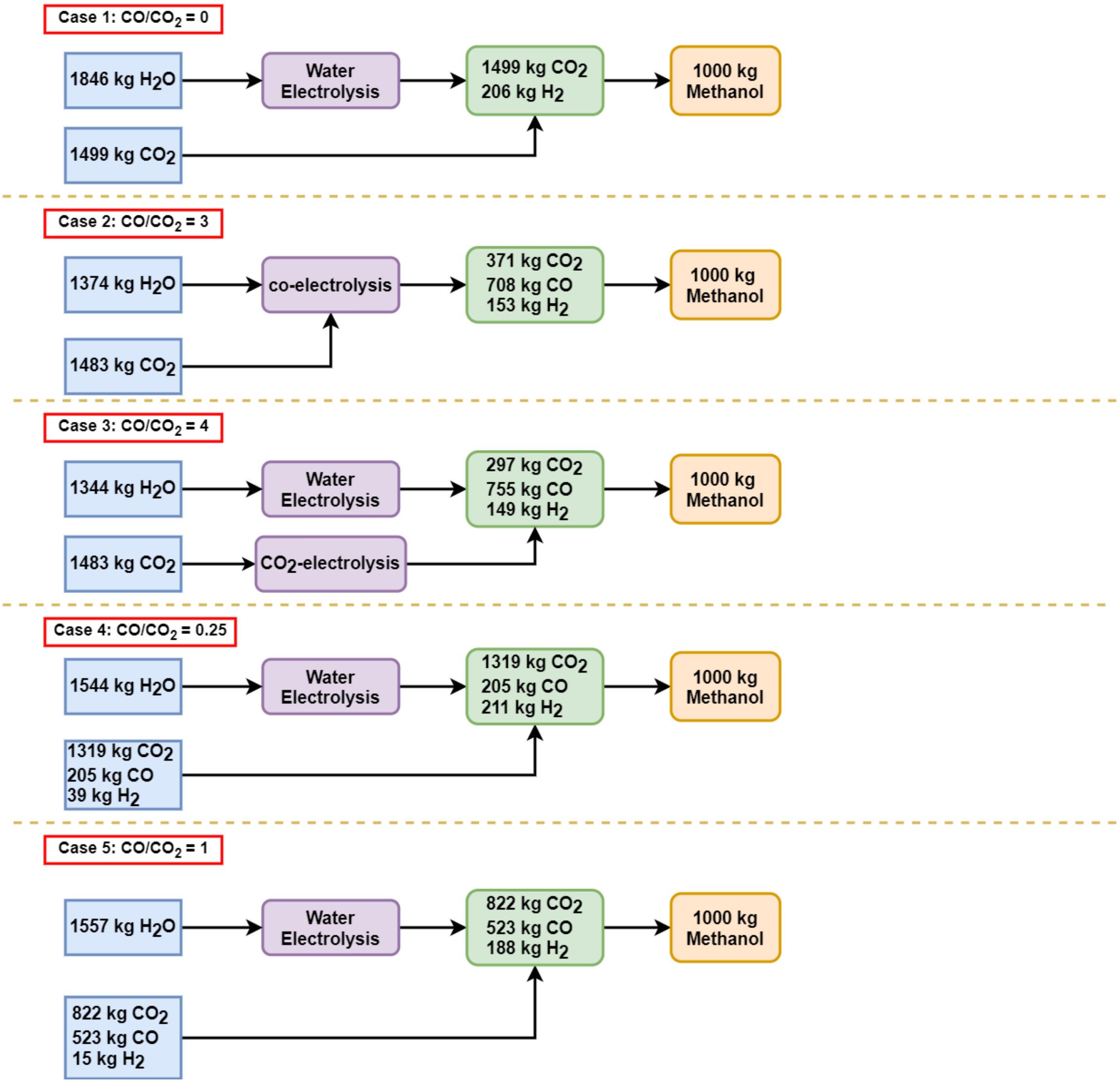

Figure 5.2: Mass balance for the five different cases with a CO/CO_2 ratio between 0-4 defined in Chapter 3. The mass balances are based on a production of 1000 kg of methanol

Besides the costs for the feedstock, other costs that contribute to the total methanol cost price are: removal costs of CO_2/inert species, CAPEX investments for equipment and additional costs for labour for example. A typical value used for the CAPEX in chemical processes is 20% of the operational expenditure (OPEX) [15]. Additional costs are assumed to be 10% of the utility costs, which are defined in Eq. 5.2. All steps in the calculation are shown in Eqs. 5.2-5.6.

$$\begin{aligned}\text{Utility costs PEM} = {} & (\text{Electrolysis costs}) + (\text{CO}_2/\text{inert removal costs}) \\ & + (\text{Methanol plant auxiliary costs}) + (\text{Added CH}_4\text{ costs})\end{aligned} \tag{5.2}$$

$$\text{Additional costs} = \text{Utility costs} \times \text{Additional cost share} \tag{5.3}$$

$$\text{OPEX} = \text{Utility costs} + \text{Additional costs} \tag{5.4}$$

$$\text{CAPEX} = \text{OPEX} \times \text{CAPEX share} \tag{5.5}$$

$$\text{Methanol price} = \text{OPEX} + \text{CAPEX} \tag{5.6}$$

The TG and BFG are burned in the conventional processes and generate heat that is integrated in the SMR or steel manufacturing process, respectively. Therefore, cases 4 and 5, with CO/CO_2 ratios of 0.25 and 1, respectively, require the addition of extra heat. To obtain extra heat, additional CH_4 is bought, which increases the methanol cost price. The amount of CH_4 (ADD_{CH_4}) is calculated with Eq. 5.7 by subtracting the lower heating value (LHV) of the CO_2-lean stream (LHV_{lean}) from the LHV of the TG/BFG (LHV_{TG}/LHV_{BFG}) stream and dividing it by the LHV for CH_4 (LHV_{CH_4}).

$$ADD_{CH_4} = \frac{(LHV_{BFG} - LHV_{lean})}{LHV_{CH_4}} \tag{5.7}$$

Before the methanol cost price can be determined, all necessary parameters and energy and mass flows need to be defined. These can be obtained from the simulated model, assumptions and literature data. An overview of the relevant factors is given in Table 5.2. The electrolysis parameters were defined in Chapter 1 and Chapter 2 and the capture costs, electricity price and steam price were defined in Chapter 4.

Table 5.2: Relevant parameters for the methanol cost price calculation

Cost parameters			
Constant	value	unit	description
$C_{capture}$	35	€/t	price per ton capture of CO_2, CH_4 and N_2
$C_{electricity}$	40	€/MWh_e	Electricity price
C_{steam}	30	€/MWh	Steam price per MWh
CAPEX/OPEX	0.2	[-]	CAPEX/OPEX ratio of 20:80
ACS	0.1	[-]	Additional cost share
Electrolysis parameters			
Constant	value	unit	description
PEM_{H_2}	55	MWh_e/t_{H_2}	Power consumption to produce 1 ton of H_2 using PEM
$SOEC_{H_2}$	42	MWh_e/t_{H_2}	Power consumption to produce 1 ton of H_2 using SOEC
TH_{CO}	8.0	MWh_{th}/t_{CO}	Thermal power consumption to produce 1 ton of H_2 using SOEC
PC_{CO}	5.0	MWh_e/t_{CO}	Electrical power consumption to produce 1 ton of CO using SOEC
TH_{CO}	1.0	MWh_{th}/t_{CO}	Thermal power consumption to produce 1 ton of CO using SOEC
$PC_{co\text{-}elec}$	7.2	MWh_e/t_{CO}	Electrical power consumption to produce 1 ton of syngas (9:3:1, H_2:CO:CO_2)
$TH_{co\text{-}elec}$	1.4	MWh_{th}/t_{CO}	Thermal demand to produce 1 ton of syngas (9:3:1, H_2:CO:CO_2)
Methane cost			
Constant	value	unit	description
CH_4 MMbtu	2	$/MMbtu	Henry hub gas price in dollars per million btu
Euro/Dollar	0.9	€/$	Exchange rate Euro/Dollar
LHV_{CH_4}	50	MJ/kg	LHV methane
btu	1059	J	Energy per btu
C_{CH_4}	85	€/t	Price per ton of methane

Parameters are defined, which allow for calculation of the methanol cost price. However, the energy and mass balances of each case need to be defined first, which are presented in Table 5.3. The market price for the methane is based on the Henry Hub natural gas price [40]. Calculations for the CH_4 price are performed in more detail in Appendix B.

Table 5.3: Energy and mass balance for Case 1-5, obtained from simulations of the methanol plant model

CO_2/inert capture mass balance						
	Symbol	**Case 1**	**Case 2**	**Case 3**	**Case 4**	**Case 5**
capture rate CO2/CH4(%)		90	90	90	90	92
TG (kg)		2261	2236	2237	1790	2197
TG rest stream (kg)		762	754	754	161	771
CH_4 capture (kg)	R_{CH_4}	0	0	0	161	0
Added CH_4(kg)	ADD_{CH_4}	0	0	0	152	141
N_2 capture	R_{N_2}	0	0	0	0	771
CO_2 capture	R_{CO_2}	1499	1483	1483	0	0
Methanol plant mass balance						
CO_2 input (kg)	T_{CO_2}	1499	371	297	1319	822
CO input (kg)	T_{CO}	-	708	755	205	523
H_2 input (kg)		206	153	149	211	188
Water produced (kg)		573	128	101	454	265
MeOH produced (kg)		1000	1000	1000	1000	1000
Methanol plant energy balance						
Auxiliary energy (MWh,e)	P_{aux}	0.07	0.32	0.06	-0.11	0.31
Thermal energy (MWh,th)		-1.28	-1.68	-1.22	-2.10	-1.02
Electrolysis mass balance						
Water required (kg)		1846	1374	1344	1544	1557
H_2 produced (kg)	T_{H_2}	206	153	149	172	173
CO/CO_2 ratio (mol/mol)		0	3	4	0.25	1
O_2 produced (kg)		1640	1626	1626	1372	1384
CO produced (kg)		-	708	755	-	-
Electrolysis energy balance						
electrical Energy (MWh,e)	$P_{electrical}$	11.33	8.86	11.99	9.44	9.52
Thermal energy (MWh,th)	$P_{thermal}$	0	1.69	0.72	0.00	-
Total Energy req. (MWh)		11.33	10.55	12.71	9.44	9.52

Capture rates for the Cases 1-4 are assumed to be 90% of the CO_2/CH_4 except for case 5 where the assumption is made that 5 mol% of the N_2 remains in the carbon-rich stream. This assumption is made to prevent to high amounts of inerts from entering the reactor. All necessary data is available and the cost price of the methanol (C_{MeOH}) as function of the electricity price for each case can be calculated. Calculation for Case 1 is performed as an example in the following steps 5.8 - 5.10:

$$\text{Utility costs PEM} = (C_{electricity} \cdot P_{electrical}) + (R_{CO_2} \cdot C_{capture}) + (P_{aux} \cdot C_{electricity}) \tag{5.8}$$

$$\text{Additional costs} = \text{Utility costs} \times \text{ACS} \tag{5.9}$$

$$\begin{aligned} C_{MeOH} &= \text{Utility costs} + \text{Additional costs} + \\ &\quad (\text{Utility costs} + \text{Additional costs}) \times \text{CAPEX/OPEX} \end{aligned} \tag{5.10}$$

Steps 5.8, 5.9 and 5.10 will be slightly different for the Cases 2-5. In Cases 4 and 5 for example extra costs for added methane need to be included and in the cases where SOEC is used (Case 2 and 3) thermal energy in the form of steam costs have to be added. For each of the five cases, when using an electricity price of €40 per MWh the cost price for the methanol is calculated and shown in Table 5.4, with the respective costs for each share.

Judging from Table 5.4, in Case 4 the cheapest methanol is produced. One of the explanations is the lower energy requirement necessary in the electrolysis unit. A big advantage of Case 4 is the presence of hydrogen in the TG. This lowers the amount of hydrogen that needs to be added, and therefore the electrolysis costs. The second cheapest option is Case 5 that required similar electrical costs. However, when compared to Case

Table 5.4: Methanol (MeOH) cost price for each of the 5 cases at a CO_2 price of €35 per ton and electricity price of €40 per MWh. The different cost shares that add up to the OPEX (operational expenditure) can be seen. The total methanol cost price given in euros per ton of methanol is the sum of the OPEX and CAPEX (capital expenditure).

	Case 1	Case 2	Case 3	Case 4	Case 5
CO/CO_2	0	3	4	0.25	1
Electrolysis electrical costs	453	355	480	377	381
Electrolysis thermal costs	0	51	22	0	0
Capture costs	52	52	52	6	27
Auxiliary energy costs	3	13	2	0	12
Added CH4 costs	0	0	0	13	12
Additional costs	51	47	56	40	43
OPEX	559	517	611	436	475
CAPEX	112	103	122	87	95
Total MeOH costs (€/$t_{methanol}$	671	620	733	523	570

4, capture costs and auxiliary costs are higher and thus Case 5 is slightly more expensive than Case 4. The worst option is Case 3, which has the highest cost for electrolysis. This can be explained by the need for two separate electrolysis steps to acquire the CO/CO_2 ratio of 4, which increase the electrolysis energy demand. This can also be observed from Table 5.2.

For each case the cost for electrolysis is shown to have the biggest contribution to the total methanol cost price. At an electricity price of €40 per MWh the electrolysis share for each case accounts to more than 55 % of the total costs. Since the electrolysis steps require electricity, the electricity price is the determining factor in the methanol cost price.

Since the calculations in Table 5.4 are only performed for an electricity price of €40 per MWh, it would be interesting to see how the effect of variation in the electricity price contributes to the methanol cost price. Furthermore, this methanol price will be compared to a market price of €400 per ton of methanol [39]. Figure 5.3 shows the methanol cost price for each case as a function of the electricity prices.

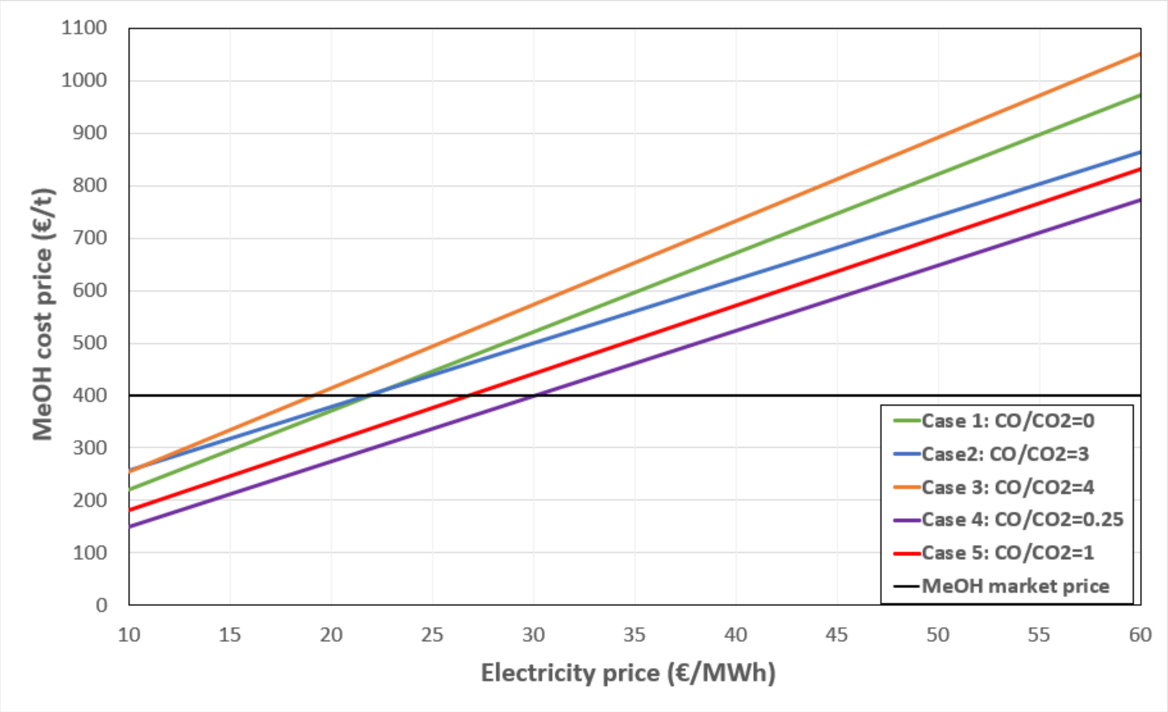

Figure 5.3: Methanol cost price versus electricity price for the five different cases, using PEM for the hydrogen production

The intersection points, between the graphs for each case and the methanol market price line, show what the electricity price is at which the production price is equal to the market price. This means that when the electricity price increases beyond the intersection point, cost prices will be higher than the market price and production of methanol will yield a negative profit. Again Case 4, appears to be the cheapest option as higher electricity prices are allowed for which methanol is still produced below market price. The opposite can be concluded for Case 3, which is thus the least favourable option. The electricity prices at which each case breaks even with the market price are calculated and shown in Table 5.5.

Table 5.5: Electricity at which each case breaks even with the market price of €400 per ton of methanol using PEM

	Case 1	Case 2	Case 3	Case 4	Case 5
Break even el. price (€/MWh)	22.0	21.8	19.1	30.1	26.9

Based on the break even (BE) electricity price in Table 5.5, Case 4 is the cheapest option as methanol production is still feasible at a higher electricity price, compared to the other cases. Which is based on a market price of €400 per ton of methanol. Case 3 is the worst option judging from the lowest break even electricity price.

5.2.2. Hydrogen from SOEC

In the same way as in the previous section the methanol cost price can be calculated using hydrogen produced with SOEC water electrolysis. Assumed is that SOEC electrolysis has the same lifetime and CAPEX investments costs as PEM. The big difference between PEM and SOEC hydrogen production is the difference in electrical requirement and the additional heat demand needed. In this scenario the calculation step shown in Eq. 5.8, will be different, however the rest of the calculation will follow Eqs. 5.9 and 5.10. The adjusted equation for the SOEC hydrogen scenario is given in Eq. 5.11.

$$\begin{aligned}\text{Utility costs SOEC} &= (C_{\text{electricity}} \cdot P_{\text{electrical}} + C_{\text{steam}} \cdot P_{\text{thermal}}) + (R_{CO_2} \cdot C_{\text{capture}}) \\ &\quad + (P_{\text{aux}} \cdot C_{\text{electricity}}) \end{aligned} \tag{5.11}$$

The mass balance for each case remains the same and was given in Figure 5.2 and Table 5.3. However, the electrical and thermal energy requirements are different, which are shown in Table 5.6.

Table 5.6: SOEC electrical, thermal and total energy requirements for electrolysis for each case

Electrolysis energy balance						
		Case 1	Case 2	Case 3	Case 4	Case 5
electrical Energy (MWh,e)	$P_{\text{electrical}}$	8.65	8.86	10.05	7.20	7.27
Thermal energy (MWh,th)	P_{thermal}	1.65	1.69	1.91	1.37	1.38
Total Energy req. (MWh)		10.30	10.55	11.96	8.58	8.65

As can be seen from Table 5.6, electrical energy requirements are lower in case of SOEC compared to PEM, however for each case extra heat demand is required. Though, the total energy demand is lower for each case which is caused by the lower total power consumption requirement compared to PEM. The resulting methanol cost prices per case is given in Table 5.7.

Judging from Table 5.7, Case 4 is still the cheapest option and Case 3 the most expensive option. However, Case 1 is now slightly cheaper than Case 2. The methanol cost price for Case 2 remained the same, for both PEM and SOEC water electrolysis, since it uses co-electrolysis, which is solely applicable using SOEC technology. Figure 5.4 shows the dependency of the methanol cost price for electricity prices between 10-60 €/MWh for SOEC electrolysis. Again break even electricity prices can be determined which are given in Table 5.8.

Table 5.7: Methanol cost price using SOEC for hydrogen production

	Case 1	Case 2	Case 3	Case 4	Case 5
CO/CO_2	0	3	4	0.25	1
Elctroysis electrical costs	346	355	402	288	291
Electrolysis thermal costs	49	51	57	41	42
Capture costs	52	52	52	6	27
Auxiliary energy costs	18	13	14	10	26
Added CH4 costs	0	0	0	13	12
Additional costs	47	47	52	36	40
OPEX	513	517	577	394	437
CAPEX	103	103	115	79	87
Total MeOH costs (€/$t_{methanol}$	616	620	693	473	524

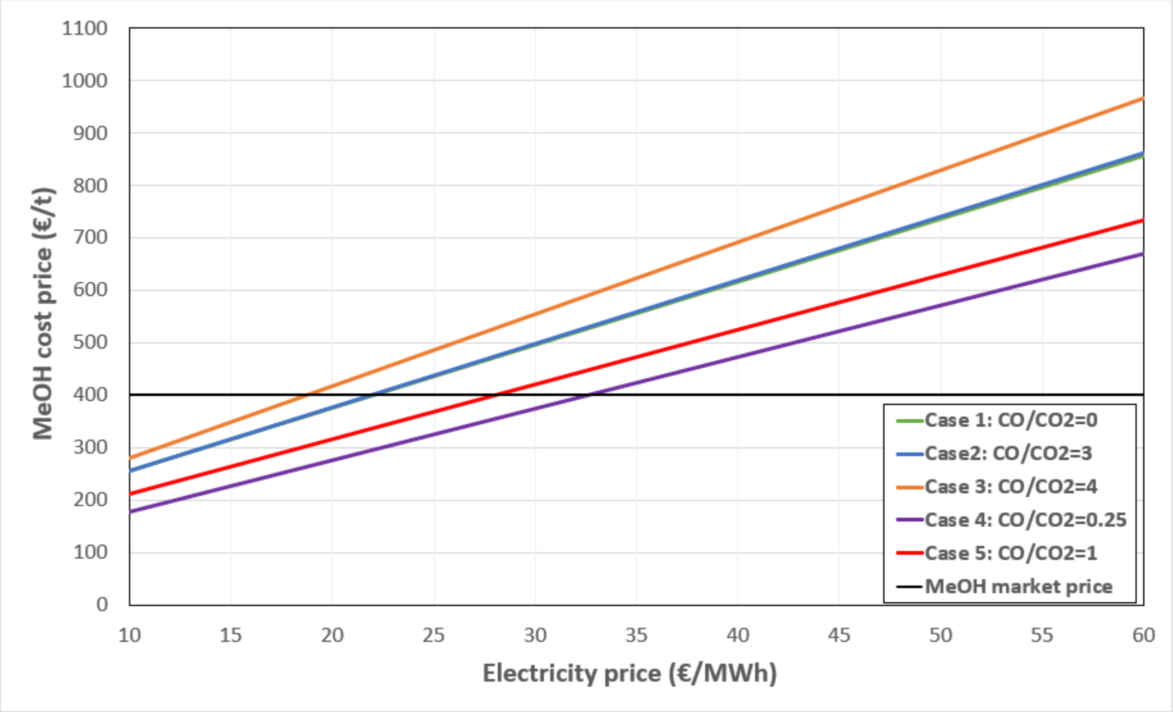

Figure 5.4: Methanol cost price versus electricity price for the five different cases, using SOEC for the hydrogen production

Table 5.8: Electricity at which each case breaks even with the market price of €400 per ton of methanol using SOEC

	Case 1	Case 2	Case 3	Case 4	Case 5
Break even el. price (€/MWh)	22.1	21.8	18.6	32.6	28.1

5.2.3. Comparison PEM and SOEC

Based on the results from sections 5.2.1 and 5.2.2 a comparison between both methanol cost prices for the two ways to produce the hydrogen, through PEM or SOEC, can be made. A first observation is that the methanol price for Case 2 is the same for both PEM and SOEC, because co-electrolysis is only an option when using SOEC. The BE electricity prices for PEM and SOEC are given in Table 5.9.

Table 5.9: Electricity at which each case breaks even with the market price of €400 per ton of methanol, PEM vs SOEC

Break even el. price (€/MWh)	Case 1	Case 2	Case 3	Case 4	Case 5
PEM	22.0	21.8	19.1	30.1	26.9
SOEC	22.1	21.8	18.6	32.6	28.1

The difference between the BE prices is biggest in cases 4 and 5, and higher for the SOEC cases, meaning that SOEC has a slightly higher range of electricity prices at which the methanol can be produced below market price. However, the differences are relatively small. This might be caused by the fact that the steam price is fixed at 30 €/MWh, so at low electricity prices the hydrogen cost share decreases more in the PEM cases, compared to the SOEC cases that also have a fixed thermal energy cost, linked to the steam price. The effect of using SOEC is more predominant when higher electricity prices are taken into account, which is obvious when comparing Figure 5.3 and Figure 5.4, where the methanol prices for PEM ranges between 1050-770 €/$t_{methanol}$ and for SOEC between 970-670 €/$t_{methanol}$ at €60 per MWh. Although case 2 and 3 require the least amount of hydrogen, they still require more electricity and heat demand due to the high need of co-electrolysis and two syngas upgrading steps, respectively.

5.2.4. Oxygen sales

The methanol cost price can be reduced when the revenues from selling oxygen are subtracted from the cost price calculated in section 5.2.1. This will only be addressed in case of PEM. Since SOEC typically requires sweep air to blow the produced air from the cathode and will not yield pure oxygen. Pure oxygen can be sold at a price between €50-80 per ton of oxygen [9, 41]. Based on these oxygen prices a new methanol cost price can be calculated for a lower case of €50 per ton of O_2 and upper case of €80 per ton of O_2.

The amount of oxygen produced in each case can be found in Table 5.3. In the calculation, Case 2 is excluded as co-electrolysis only uses SOEC electrolysis technology. For both oxygen selling prices at €50 and €80 per ton, the methanol cost prices are given in Figure 5.5 for an electricity price of 40 €/MWh.

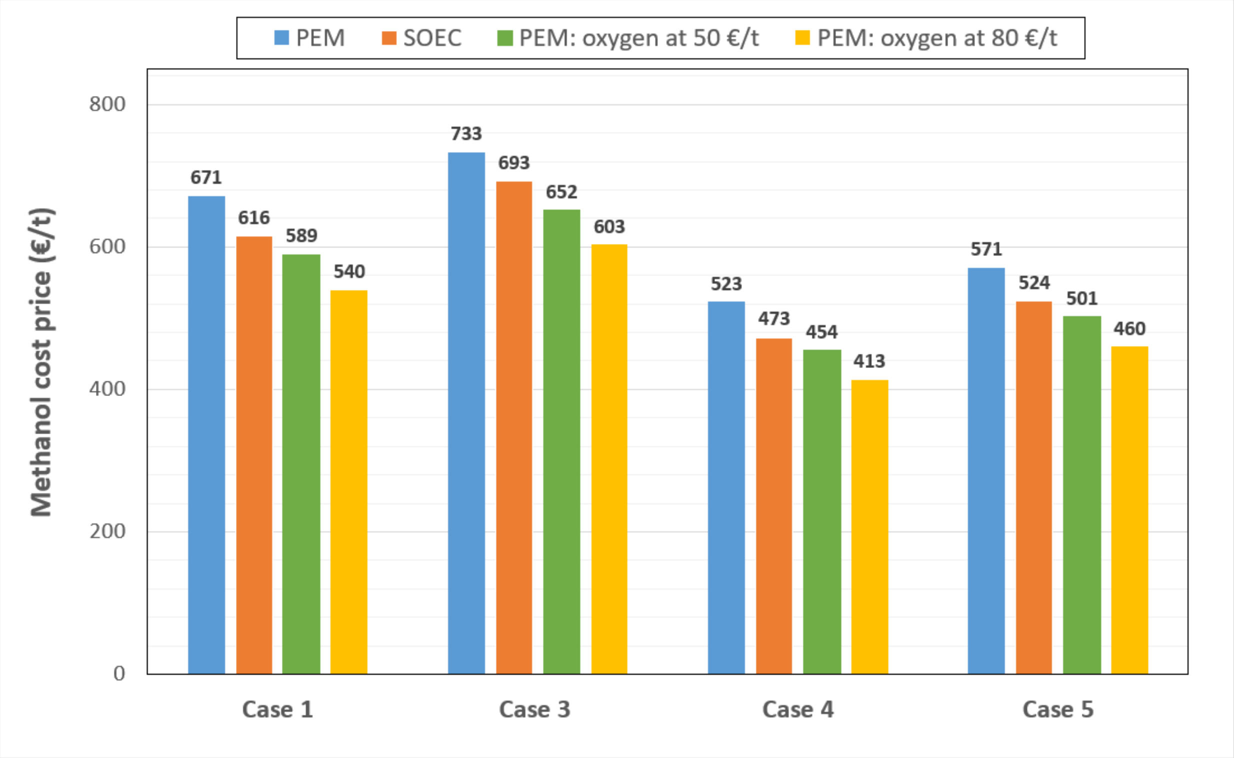

Figure 5.5: Methanol cost price in euros per ton for PEM, SOEC and PEM when selling oxygen at €50 and €80 per ton. Electricity and CO_2 prices are, €40 per MWh and €35 per ton, respectively.

For each case at the two oxygen prices, the cost price of the methanol for PEM is now lower than when using SOEC. Oxygen price thus has a big impact on the methanol cost price and will increase the BE electricity price. Which means that the production of methanol can be competitive with the market price for higher electricity prices.

5.2.5. Effect of CO/CO_2 ratio

As could be concluded from the methanol cost price calculations, a lower hydrogen requirement reduces the electrical demand, which in turn reduces the methanol cost price. Therefore, the effect of the CO/CO_2 ratio on the required amount of hydrogen to produce 1 ton of methanol is showed in Figure 5.6. It shows that for higher CO/CO_2 ratios less hydrogen is required for the methanol synthesis reaction. This is as expected when comparing the stoichiometry in the direct CO and CO_2 hydrogenation reactions, Eq. 1.20 and Eq. 1.21, that require 2 and 3 moles of H_2 to produce one mole of methanol, respectively. Another benefit of a higher CO/CO_2 ratios is that less water is produced which reduces distillation demand.

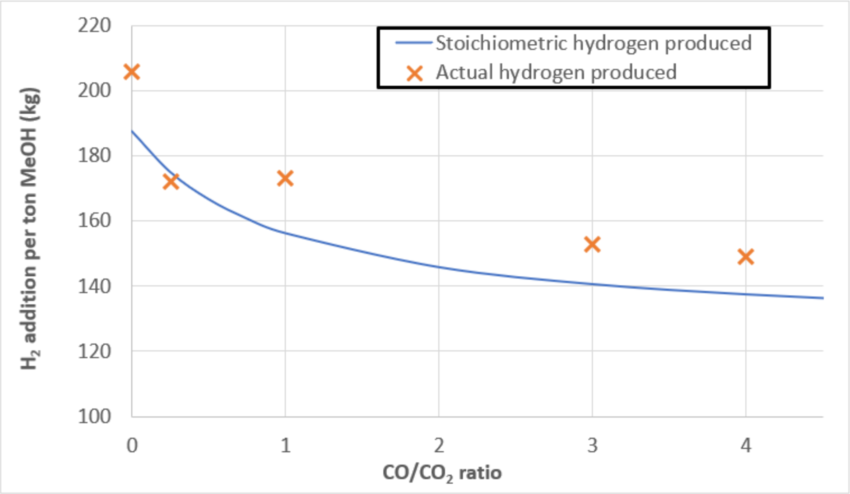

Figure 5.6: Stoichiometric amount of hydrogen that has to be added to produce one ton of methanol as function of the CO/CO_2 ratio. Orange markers represent the actual hydrogen requirement for the five Cases with CO/CO_2 ratios between 0-4, the blue line shows the stoichiometric amount of hydrogen required.

Based on Figure 5.6 Cases 2 and 3 with a CO/CO_2 ratios of 3 and 4, respectively, should be the cheapest options as they require the least amount of hydrogen. However, this does not hold, as Case 4 with a CO/CO_2 of 0.25 was found to be the cheapest case in the previous sections. In Table 5.10 some relevant parameters that can aid with the reasoning, why Case 2 is the cheapest option are given.

Table 5.10: Some important factors that determine the differences in cost price between the five cases

	Case 1	Case 2	Case 3	Case 4	Case 5
CO/CO_2 ratio	0	3	4	0.25	1
Methanol yield (%)	91.7	92.7	92.7	83.7	83.6
Required hydrogen production (kg)	206	153	149	172	173
Total energy requirement	11.33	10.55	12.71	9.44	9.52
Captured mass (kg)	1499	1483	1483	161	771

Although Case 2 and Case 3 require less hydrogen compared to case 4, they require more total energy, which results in higher electrolysis costs. Furthermore, the capture costs are higher in Case 2 and Case 3, because captured mass is almost a factor 10 times higher compared to Case 4. Besides the low electrolysis costs, the TG in Case 4 contains a relatively high amount of H_2 compared to Case 1, 2 and 3. This decreases the requirement for hydrogen production, which gives an explanation for the low electrolysis costs.

Table 5.10 shows that the hydrogen requirement is similar for Cases 4 and 5. Judging from the CO/CO_2 ratio, the hydrogen requirement for Case 5 should be lower than Case 4. However, Case 4 and 5 require similar amounts of hydrogen, with 172 and 173 kg per ton of methanol, respectively. The high hydrogen fraction in the TG stream compensates the difference in hydrogen requirements, between Case 4 and Case 5. The difference between Case 4 and 5 is therefore not determined by the hydrogen requirement, but instead by the auxiliary and capture costs. These costs are higher for Case 5, which results in an overall lower total methanol cost price for Case 4. Case 1 is less attractive because a large amount of hydrogen has to be produced per ton of methanol, compared to the other cases. Therefore, Case 1 is more expensive than Case 4 and 5.

Methanol yield of Cases 1-3 is higher than Case 4 and 5, which is caused by the higher fraction of inerts in inlet stream of the methanol plant. Higher inert fractions in the inlet stream require higher purge of the recycle streams, to avoid accumulation inside the reactor. By having a higher purge, components such as hydrogen and carbon species also get purged. However, the lower yield in Cases 4 and 5 does not have a large influence on the cost price.

Case 4 is the cheapest option, based on a couple of aspects:

1. A high presence of hydrogen in the TG lowers the required amount of H_2 that has to be added. Resulting in even lower hydrogen production compared to Case 5, even though Case 5 has a higher CO/CO_2 ratio.
2. Low capture requirements in terms of mass (161 kg), which results in relatively low costs required for capture/removal.
3. Auxiliary energy requirements are low, which results in a respective low energy cost.

The least favourable options are Case 1, Case 2 and Case 3, for which a couple of explanations can be given:

- Case 1, $CO/CO_2 = 0$
    1. Low CO/CO_2 ratio and therefore large production of hydrogen is required per ton of methanol.
    2. High capture costs, due to 1499 kg CO_2 capture requirement.
- Case 2, $CO/CO_2 = 3$
    1. High energy requirements are needed. Co-electrolysis is a relatively new SOEC technology at a max scale of 10 kW [24]. Therefore, improvements can be made reducing the energy requirements in the future.
    2. High capture costs, due to 1483 kg CO_2 capture requirement
- Case 3, $CO/CO_2 = 4$
    1. Two electrolysis steps, CO_2 electrolysis and water electrolysis, are required to get the correct CO/CO_2 of 4. This increases the electrolysis energy demand and makes it the least feasible of the five cases.
    2. High capture costs, due to 1483 kg CO_2 capture requirement

5.3. Fischer-Tropsch

As mentioned in Section 1.5.3 a range of products can be produced through FT synthesis, which are NGL, gasoline, diesel and waxes. The conventional pathway to produce FT products requires a H_2/CO syngas, which is typically obtained from the reforming of fossil fuels. However, there is a way to operate the process with renewable energy sources by shifting the production of syngas to electrolysis technology combined with one the CO_2 capture sources described in Section 4.5. CO_2 electrolysis could be a solution to supply the carbon monoxide, whereas water electrolysis can supply the hydrogen. When syngas is produced through CO_2 electrolysis and water electrolysis the cost price is mostly dependant on the electricity.

In this Section the marginal cost price for the production of the FT product will be calculated using a H_2/CO ratio equal to 2.00, which also means a SR equal to 2. Furthermore, the feasibility of producing FT products by syngas produced from electrolysis will be assessed. Therefore, the marginal cost price, based on the feedstock cost is compared to the market price for the product. In this way an initial estimate can be made on the competitiveness of the renewable FT production route, compared to the conventional production route. Furthermore, the effects of electricity price and CO_2 price variations will be assessed with respect to the required product composition. The schematic of the FT synthesis process with carbon capture, H_2 production and conversion to FT liquids is shown in Figure 5.7.

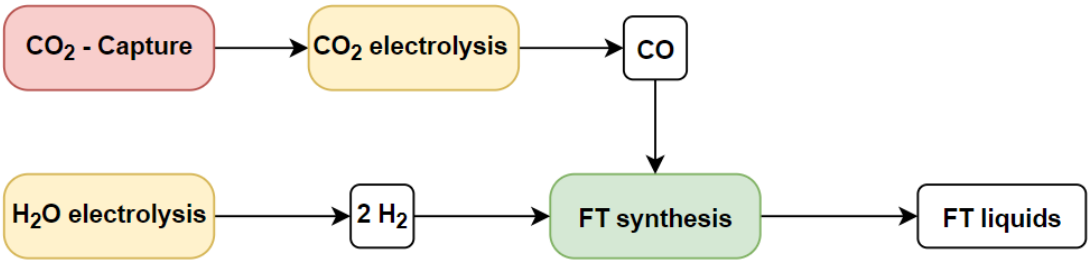

Figure 5.7: Schematic of the FT process, showing CO_2 capture and conversion to CO using SOEC CO_2 electrolysis. Hydrogen is produced using water electrolysis. A 2:1 ratio of H_2:CO enters the FT synthesis reactor.

5.3.1. Gross profit analysis

The starting point for the economic analysis performed in this section is a pure stream of CO_2. The pure CO_2 can be capture from any of the high partial pressure sources, namely TG, BFG or biogas, defined in Chapter 3. To produce FT liquids from CO_2, a combination of SOEC CO_2 electrolysis and PEM electrolysis is used. Power consumption for PEM and SOEC CO_2 electrolysis are based on the values defined in Section 1.4 and Chapter 2, respectively. The syngas produced by electrolysis will contain H_2 and CO in a ratio of 2:1. A 2:1 ratio of H_2:CO, means the SR is fixed at 2, which was also the case for the methanol synthesis process. The relevant parameters required for the cost calculations are given in Table 5.11. Besides the parameters required for the calculation of the FT product price, Table 5.11 also shows the prices at which the FT products can be sold. It is assumed that the sales from the wax fraction are 10 times higher than the sales from the other NGL, gasoline and diesel fractions.

For a few products with increasing molecular mass, the mass balances and prices for the CO_2 and hydrogen shares that sum up to the total cost for the syngas required to produce 1 ton of product, are given in Table 5.12. This cost price is only based on the prices for the feedstock. Investment costs, labour costs and depreciation costs are all factors that would increase the price, but are not taken into account here. Based on the data from Table 5.11, the hydrogen price is 2200 €/t, for a 40 €/MWh electricity price. The CO_2 price is set to 50 €/t which results in a CO price of 309 €/t.

As can be concluded from the prices in Table 5.12 the required syngas cost per ton of FT product is around € 1240. This cost price is based on full conversion of the syngas and will increase when conversion is less than 100 %. Calculation of the syngas costs ($SGC_{product}$) for the production of one ton of product is based on Eq. 5.12.

$$SGC_{product} = \frac{(PC_{H_2} \cdot M_{H_2} + PC_{CO} \cdot M_{CO}) \cdot C_{electricity} + TH_{CO} \cdot M_{CO} \cdot C_{steam} + M_{CO_2} \cdot M_{CO} \cdot C_{CO_2}}{M_{product}} \tag{5.12}$$

Table 5.11: Parameters required for the calculation of the cost price for FT products.

Parameters			
Constant	value	unit	description
C_{CO_2}	50	€/t	CO_2 price per ton range based on different source
$C_{electricity}$	40	€/MWh_e	Electricity price in euros per MWh
C_{steam}	30	€/MWh_{th}	Steam price in euros per MWh
PC_{H_2}	55	MWh_e/t_{H_2}	Total power consumption to produce 1 ton of H_2 using electrolysis
PC_{CO}	5.0	MWh_e/t_{CO}	Electrical power consumption to produce 1 ton of CO using electrolysis
TH_{CO}	1.0	MWh_{th}/t_{CO}	Thermal power consumption to produce 1 ton of CO using electrolysis
Mass balance			
Constant	value	unit	description
H_2/CO	2:1	[-]	hydrogen/carbon monoxide mol ratio of feed
M_{CO}	0.875	ton	ton CO per ton syngas
M_{H_2}	0.125	ton	ton H_2 per ton syngas
$M_{product}$	0.440	ton	ton FT product per ton syngas
M_{CO_2}	1.571	ton	ton CO_2 required per ton CO
Fischer-Tropsch parameters			
Constant	value	unit	description
P_{NGL}	0.5	€/L	Selling price for natural gas liquids fraction (C_2-C_4)
P_{gas}	0.5	€/L	Selling price for gasoline fraction (C_5-C_{11})
P_{diesel}	0.5	€/L	Selling price for diesel fraction (C_{12}-C_{19})
P_{wax}	5	€/L	Selling price for wax fraction (C_{20+})
ρ_{NGL}	0.65	kg/L	Density natural gas liquids fraction
ρ_{gas}	0.75	kg/L	Density gasoline fraction
ρ_{diesel}	0.85	kg/L	Density diesel fraction
ρ_{wax}	0.95	kg/L	Density wax fraction

To make the comparison between production costs and revenues from sales of the FT products, prices are compared on a barrel (bbL) of oil equivalent. One bbl contains 159 litres of product. This is a convenient measure as oil market prices are typically available on bbl basis. The syngas cost will be compared to the revenues from selling the product and to the conventional bbl cost produced at oil refineries, for which the following assumptions are made:

- Price for oil on the market is €40 per bbl [2]
- Refining costs are €25 per bbl
- Total price for a bbl of oil is €65
- The selling prices for the NGL, diesel and gasoline factions are equal to €0.5 per litre product, which equals a revenue of €79.5 per bbl
- The selling price for the wax fraction is equal to €5.0 per litre product, which equals a revenue of €795 per bbl

Table 5.12 clearly shows, that the syngas cost price for each product is similar and irrespective of the product on a mass basis. However, on a bbl basis the prices show some variation, since each product fraction has different densities.

Judging from the calculations in Table 5.12, depending on the product, production costs vary between €150-189 per bbl of FT product. These prices were calculated for a CO_2 price of € 50 per ton and an electricity price of € 40 per MWh. Lower feedstock costs, would decreases the FT product cost price. Compared to the FT production cost, if only the NGL, diesel and gasoline fractions are produced at a selling price of €79.5 per bbl, a negative profit will be made. This means that on average the production cost per barrel is twice as high as the respective revenues. Furthermore, the production cost per bbl is almost a factor 2.5-3 times higher than the conventional production route, which yields a €65 per bbl cost. Since the wax fraction can be sold at €795 per bbl, higher wax fractions are desired to increase the value of the FT product. This means that in order to

Table 5.12: Syngas cost price for different product fractions in euros per barrel of FT liquid, which is the equivalent of 159 litres of product

C5							
reaction	$5CO$	+	$11H_2$	$\longrightarrow$	C_5H_{12}	+	$5H_2O$
per ton syngas	864 kg		136 kg		444 kg		556 kg
per ton product	1944 kg		306 kg		1000 kg		1250 kg
Cost per ton product	€600	+	€672	=	€1272		
Cost per bbl	**152 €/bbl**						
C10							
reaction	$10CO$	+	$21H_2$	$\longrightarrow$	$C_{10}H_{22}$	+	$10H_2O$
per ton syngas	870 kg		130 kg		441 kg		559 kg
per ton product	1972 kg		296 kg		1000 kg		1268 kg
Price per ton product	608 €	+	651 €	=	€1259		
Cost per bbl	**150 €/bbl**						
C15							
reaction	$15CO$	+	$31H_2$	$\longrightarrow$	$C_{15}H_{32}$	+	$150H_2O$
per ton syngas	871 kg		129 kg		440 kg		560 kg
per ton product	1981 kg		292 kg		1000 kg		1274 kg
Price per ton product	€611	+	€643	=	€1255		
Cost per bbl	**170 €/bbl**						
C50							
reaction	$50CO$	+	$101H_2$	$\longrightarrow$	$C_{50}H_{102}$	+	$50H_2O$
per ton syngas	874 kg		126 kg		438 kg		562 kg
per ton product	1994 kg		288 kg		1000 kg		1282 kg
Price per ton product	€615	+	€633	=	€1248		
Cost per bbl	**189 €/bbl**						

make a profit for this feedstock costs, there should be a certain wax fraction in the product. Therefore, the required amount of wax fraction in the product to break even with the production price will be assessed in the next section.

5.3.2. Electricity and CO_2 price variation

As mentioned in the previous section the production costs of FT liquids can be compared to the revenues. The FT product prices showed production could not always be profitable. A certain wax fraction is in some cases necessary to increase the revenues and make a profit. The comparison between production cost and selling price is assessed in two ways:

1. By keeping the CO_2 price constant and varying the electricity price.
    - Electricity price is varied between 10 €/MWh and 100 €/MWh
    - CO_2 price is fixed at 50 €/ton
2. By keeping the electricity price constant and varying the CO_2 price, which reflects the different capture methods discussed in Section 1.3.
    - Electricity price is fixed at 50 €/MWh
    - CO_2 price is varried between 10 - 100 €/ton

For each CO_2 and electricity price a wax fraction exists, at which the revenues from the FT products are equal to the production cost of the syngas. Besides waxes, non-waxes are taken as the average of the C_2-C_{19} products for which density and selling price for the gasoline fraction is used. Equation 5.13 shows the comparison in mathematical form, with W_f the wax fraction. The required constants and variables can be found in Table 5.11.

$$\mathrm{SGC}_{\mathrm{product}} = \left(\frac{\mathrm{P}_{\mathrm{wax}}}{\rho_{\mathrm{wax}}} \cdot \mathrm{W}_f + \frac{\mathrm{P}_{\mathrm{gas}}}{\rho_{\mathrm{gas}}} \cdot (1 - \mathrm{W}_f)\right) * 10^3 \tag{5.13}$$

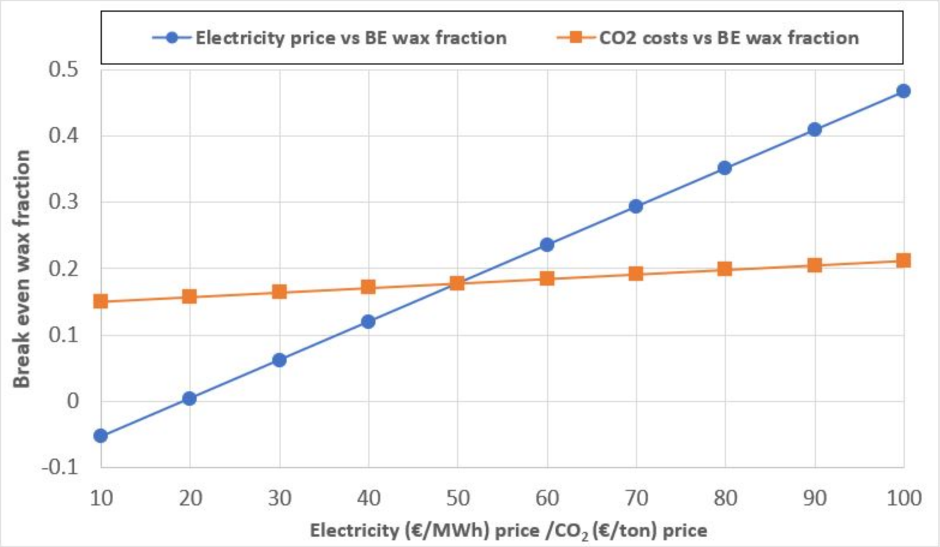

Figure 5.8: Wax fraction as a function of the electricity and CO_2 prices. The lines represent, what wax fraction is required to break even with the syngas cost price needed to synthesize the product.

The break even (BE) wax fraction can be computed when solving for W_f in Eq. 5.13. The BE wax fraction as a function of electricity price at fixed CO_2 price and as function of CO_2 price at fixed electricity price is shown in Figure 5.8. What can be concluded from Figure 5.8 is that a change in electricity price has a bigger impact on the required wax fraction, compared to a change in CO_2 price. This can be concluded by the difference in slope for both lines as the electricity/CO_2 price increases. For each increment in electricity price or CO_2 price, the wax fraction required to break even with the costs for the syngas increases. However, this increase is more significant as a function of electricity price, due to a higher required wax fraction for each increment.

In reality the BE wax fraction will be higher, because in Figure 5.8 only the costs for feedstock are considered. Additional costs and capital investments (CAPEX) should be taken into account, to get more correct values. However, this calculation was meant to show that even when these factors are not considered, renewable production of FT liquid is relatively expensive compared to the conventional barrel price at oil refineries of €65. Production of solely the non-wax fractions, will only be feasible at low electricity and CO_2 prices. When looking at the variation of the electricity price, the price should be below €20 per MWh. At higher electricity prices, waxes are a requirement in the FT product in order to make a profit. However, profits are already low based on the marginal cost price, and will be even lower when taking additional cost factors into account.

6

Conclusion

CCU processes are effective in mitigating emissions of green house gases by converting the captured carbon species into other chemicals. At the same time when excess electricity is available, electricity can be stored in liquid energy carriers, such as methanol or FT liquids. Hydrogen can be produced using electrolysis, in conjunction with renewable energy sources, such as wind, solar and hydro power. This allows for the production of renewable methanol and FT liquids.

In this thesis several different pathways were defined based on two gas streams, TG from SMR and BFG from the steel production process. These streams contain high carbon fractions with up to 60 mol % CO_2 and CO. For these two carbon-rich streams several cases could be defined based on the CO/CO_2 ratio in the syngas. A higher CO/CO_2 ratio is beneficial as no water will be produced in direct CO hydrogenation reaction to methanol. Another benefit is that direct CO hydrogenation requires less hydrogen per ton of methanol, compared to direct CO_2 hydrogenation. Using PEM and SOEC electrolysis to supply the hydrogen/upgrade the syngas, a comparison was made between five cases based on the methanol cost price. The five cases had CO/CO_2 ratios of 0, 0.25, 1 ,3 and 4, respectively.

The power consumption of PEM electrolysis was based on available data from literature and manufacturers, which was presented in Tabel 1.3. For SOEC an additional heat demand is required as preheating is necessary. However, no data was found in literature on values for this thermal demand. Therefore, using a simple reference model from literature by Samavati et al., water electrolysis with SOEC was modeled to acquire this heat demand [51]. For water electrolysis a thermal demand of 8 kWh per kg of hydrogen was found, which was equal to 19 % of the electrical power consumption.

Methanol cost price analysis

A methanol plant was modelled using a reference model from literature to acquire the mass and energy balances needed for the calculation [59]. The methanol cost price is calculated, using feedstock costs, such as CO_2 price, hydrogen price and electricity price defined in Chapter 4. The cost price is determined by the OPEX and CAPEX. The OPEX takes in to account the costs for daily operation, such as electrolysis costs, labour costs and capture costs. Whereas the CAPEX defines the capital investments and is calculated from the OPEX by using a CAPEX/OPEX ratio defined in literature [15]. A comparison between PEM and SOEC water electrolysis was performed, showing SOEC to be the cheaper option due to lower total energy demand per kg of hydrogen. However, this was based on SOEC electrolysis having the same lifetime and investment costs as PEM electrolysis.

The sales of the produced oxygen in the electrolysis reaction showed to have a big impact on the methanol cost price. The revenues from the oxygen were only considered when using PEM electrolysis, because SOEC typically requires sweep air to blow of the air at the anode, and therefore will not yield pure oxygen. Methanol cost prices for PEM electrolysis already showed lower prices at a selling price of €50 per ton of O_2, compared to the SOEC electrolysis cases.

The methanol cost price was plotted as a function of the electricity price. Case 4, with a CO/CO_2 ratio equal to 0.25, was the cheapest option followed by case 5 with CO/CO_2 is 1. For each case, the cost affiliated by electrolysis had the biggest share in the methanol cost price. Where the electrolysis costs included both electrical and thermal energy costs. One of the explanations can be found in the high electrical energy demand required for the production of one kilogram of hydrogen by electrolysis. Therefore, the electricity price had the biggest impact on the methanol cost price. Based on the CO/CO_2 ratio as a function of the required amount of hydrogen, cases with a higher ratio require less addition of hydrogen to produce one ton of methanol. This should mean that in theory Case 2 and Case 3 should be the cheapest options, because these had the highest CO/CO_2 ratio of 3 and 4, respectively. However, this does not hold, as Case 4 has the cheapest methanol cost price with just a CO/CO_2 of 0.25. There are multiple reasons why Case 4 is the best option in terms of the methanol cost price:

- Compared to the other cases, Case 4 already contains a relatively high fraction of hydrogen in the syngas originating from the TG. The presence of this hydrogen, means less H_2 has to be produced, which lowers the electrical demand for Case 4.
- Compared to the other cases, Case 4 requires the least amount of mass to be removed, which ensured a low capture cost share.
- Although Case 5 requires the same addition of hydrogen as Case 4, capture costs and auxiliary costs are lower for Case 4. Therefore, Case 4 resulted in the cheapest case.

Cases 1, 2 and 3 turned out to be the most expensive options, because of the high shares in electrolysis costs, as well as high capture costs. The reason for the higher methanol cost price compared to Case 4 and 5 had multiple reasons, depending on the case:

- Case 1, with a $CO/CO_2 = 0$, required the highest amount of hydrogen production per ton of methanol.
- For Case 2, with a $CO/CO_2 = 3$, electrolysis costs where high due to high demand per kg of syngas for co-electrolysis.
- For Case 3, with a $CO/CO_2 = 4$, two separate electrolysis steps are required to obtain the correct CO/CO_2 ratio.

Fischer-Tropsch cost price analysis

Besides the techno-economics of CCU to methanol, FT liquids can also be produced using CO_2 rich streams. Different liquid fractions are produced in the FT synthesis such as NGL, gasoline, diesel and waxes. Since the fraction of waxes yield the biggest revenue as a result of the highest selling price compared to the other FT fractions, the goal is to maximize this share in the product. At higher chain growth probabilities increasing wax fractions were present in the product stream. For the FT synthesis a H_2/CO ratio of 2 is required, which is the same as a SR of 2. The starting point is a pure CO_2 stream, originating from the TG, BFG or biogas, which is converted to CO using SOEC CO_2 electrolysis. Hydrogen is produced from water electrolysis. The cost price of the FT products is determined by calculating the marginal cost price. This represents the cost price of the required hydrogen and CO_2 to produce one ton of FT product. The feasibility of the FT products is compared in two different ways: (1) Fix CO_2 price but change electricity price and (2) fix electricity price and change CO_2 price. To check the influence of both variations, the minimum wax fraction was calculated at which the production costs equal the revenues. One of the conclusions was that electricity price had a bigger impact on the total cost price of the FT liquids, than CO_2 price. Another remark is that when producing solely diesel this way, it will not be competitive anymore unless electricity prices drop below 20 €/MWh. However, these electricity prices will have to drop even further, if additional costs are included, such as CAPEX, labour and depreciation etc.

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A

Electrochemical reduction of CO_2

Electrochemical CO_2 reduction (ECR) is yet another option to mitigate CO_2 through electrocatalytic conversion to different products [64]. Through the different pathways, by transfer of electrons reduction products, like carbon monoxide, formic acid (HCOOH), methane (CH_4) and methanol, can be obtained. Table A.1 shows some of the overall reactions to produce a selection of products. One of the important factors in ECR is the faradaic (FE) efficiency, which reflects the selectivity of the process towards the specified product [64].

Table A.1: Some electrochemical CO_2 reduction products with the respective overall reactions

Product	Overall reaction
Carbon monoxide	$CO_2 \longrightarrow CO + \frac{1}{2}O_2$
Formic acid	$CO_2 + H_2O \longrightarrow HCOOH + \frac{1}{2}O_2$
Methanol	$CO_2 + 2H_2O \longrightarrow CH_3OH + \frac{3}{2}O_2$
Methane	$CO_2 + H_2O \longrightarrow CH_4 + 2O_2$
Ethylene	$2CO_2 + 2H_2O \longrightarrow C_2H_4 + 3O_2$

Tabel A.2 shows for different C1-C2 products the number of electrons required ($\#e^-$), the theoretical voltage (V_{th}) at which the reactions start to run based on the Gibbs free energy at 298K and faradaic efficiencies (FE), from literature. The operating voltage (OV) is the theoretical voltage plus an applied overpotential, which can also be found in table A.2.

Table A.2: Some electrochemical CO_2 reduction products with the respective number of electrons, theoretical voltage, Faradaic efficiency (FE) and operating voltage (OV).

product	Number of electrons $\#e^-$ [-]	Theor. voltage V_{th} [V]	FE [%]	OV V_{op} [V]
Carbon monoxide (CO)	2	-1.33	92[64]	-1.85
Formic acid (HCOOH)	2	-1.83	89 [64]	-3.03
Methanol (CH_3OH)	6	-1.21	71 [64]	-1.53
Methane (CH_4)	8	-1.06	80 [64]	-2.06
Ethylene (C_2H_4)	12	-1.15	46 [64]	-1.66

With the theoretical and operating voltages an overall energy efficiency can be defined according to Eq. A.1 [36].

$$\eta_{overall} = FE \cdot \frac{V_{th}}{V_{op}} \tag{A.1}$$

The power requirements (E_{ECR}) in kWh to produce one ton of the products can be determined with Eq. A.2, where F is the Faraday constant and N_{CO_2} the required mole of CO_2 per ton product.

$$E_{ECR} = \frac{N_{CO_2} \cdot \#e^- \cdot F \cdot V_{th}}{3.6E6 \cdot \eta_{overall}} \tag{A.2}$$

The product price (C_{ECR}) can then be calculated based on the required amount of CO_2 combined with the electricity required with a certain electricity price ($C_{electricity}$) using Eq. A.3, with C_{CO_2} the CO_2 price per ton and T_{CO_2} the required amounts of ton CO_2 per ton of product.

$$C_{ECR} = E_{ECR} \cdot C_{electricity} + C_{CO_2} \cdot T_{CO_2} \tag{A.3}$$

Table A.3: Constants required in calculation of the cost price for ECR products

constant	symbol	Value	units
Faraday constant	F	96486	[C/mol]
Electricity price	$C_{electricity}$	30	[€/MWh]
CO_2 price	C_{CO_2}	50	[€/ton]

With the data for the constants given in Table A.3, the cost prices for the products for ECR can be calculated using Eq. A.2 and A.3 and is given in Table A.4.

Table A.4: Electrochemical CO_2 reduction cost price of products in euros per ton of product

Electrochemical CO_2 reduction product price						
product	M_m [g/mol]	#e^- [-]	T_{CO_2} [$t/t_{product}$]	N_{CO_2} [$mol/t_{product}$]	E_{ECR} [kWh]	C_{ECR} [€/$t_{product}$]
CO	28	2	1.57	92[64]	$3.84 \cdot 10^3$	231
HCOOH	46	2	0.96	89 [64]	$3.04 \cdot 10^3$	206
CH_3OH	32	6	1.38	71 [64]	$1.13 \cdot 10^4$	503
CH_4	16	8	2.75	80 [64]	$3.44 \cdot 10^4$	1518
C_2H_4	28	12	3.14	46 [64]	$4.18 \cdot 10^4$	1815

B

Methane cost price analysis

Based on Seider and Seeder a first indication of the economic feasibility of products can be given using marginal cost price analysis [53]. As can be seen from Table 4.8 the marginal cost price for production of methane at an electricity price of 40 €/MWh and CO_2 cost of 50 €/ton, was almost €1240 per ton of methane. This will be compared to some other cases and routes to produce methane. As was shown in Appendix A, electrochemical reduction of CO_2 also yielded a price of 1520 €/ton methane.

The market price for methane is typically given in dollars per million British thermal units, $/MMBtu, and is dependent on location. Prices in the USA are based on the Henry Hub natural gas price. Over the year 2019 the Henry Hub natural gas price varied between 1.7 and 2.0 $/MMBtu [40]. However, in other parts of the world in Qatar for example lower natural gas prices exist in the order of 0.7-1.0 $/MMBtu. Three natural gas market price ranges for the Middle East, USA and Europe are given in Table B.1. Prices for the European market are higher, due to the need to import it from russia. Furthermore, Table B.1 shows the conversion factors from Dollar to Euro, from MMBtu to Joules and from €/MMBtu to €/ton methane.

Table B.1: Methane market price and the required conversion parameters for three different markets: Middle East, USA and Europe. Market prices are given in dollar per million British thermal units and calculated in Euros per ton of CH_4

Parameters and constants		
Joules per Btu	1059	J/Btu
Joules per MMBtu	$1.06 \cdot 10^9$	J/MMBtu
LHV per ton CH_4	$5.0 \cdot 10^{10}$	Joules/t,CH_4
MMBtu per ton CH_4	47.2	MMBtu/t,CH_4
Dollar/Euro exchange rate	0.9	$/€

Methane market price						
	$/MMBtu			€/ton		
Location	range	Low	High	Low	High	average
Middle-east (Qatar)	0.7-1.0	0.63	0.9	29.7	42.5	36.1
Henry Hub (USA)	1.7-2.0	1.53	1.8	72.2	85.0	78.6
Europe	-	3.0	3.5	141.6	165.3	153.4

As can be seen from Table B.1 the market price for methane has a strong dependency on location. The average price ranges from 36 €/ton in the Middle East to 153 €/ton for Europe.

When comparing these market prices with the methane cost prices calculated by hydrogenation of CO_2 (1238 €/ton) and ECR (1520 €/ton), cost prices are a factor 10 times more expensive compared to the average market price in Europe and more than 30 times the market price compared to the Middle East. The cost prices are based on the marginal cost price. The cost price will increase further when the efficiency of the process is included. With a lower efficiency the cost price increases as extra feedstock is required to produce the same amount of methane. Typical efficiencies for methanation reaction based on the LHV are between 75-85 % [10], therefore an efficiency of 80 % is assumed.

Besides the efficiency other factors that increase the cost price are:

1. CAPEX costs reflecting the capital investment costs, which is assumed as 20 % of the marginal cost price.
2. Depreciation costs which is assumed to be 15 % of the marginal cost price
3. Downstream processing costs which represent 10 % of the marginal cost price

These additional costs are summarized and given in Table B.2, together with the relevant parameters needed for the cost price analysis of methane.

Table B.2: Calculation parameters required for methane cost price analysis

$C_{electricity}$	40	€/MWh	electricity price
C_{CO_2}	50	€/t	CO_2 price
PC_{H_2}	55	€/MWh	power requirement per kg of hydrogen
η	0.8	[-]	Efficiency of the methanation process
DE	0.15	[-]	depreciation share of the marginal costs
CAPEX	0.20	[-]	CAPEX share
DP	0.10	[-]	Downstream processing costs share
C_{H_2}	2200	€/t	hydrogen cost per ton

The methane price calculated in Table 4.8 was equal to €1238 per ton of methane. This cost price is recalculated, while considering the additional cost shares mentioned. The cost price of the methane is calculated in different steps in Table B.3 using the parameters defined in Table B.2. All prices are based on the production of one ton of methane.

Table B.3: Calculation of the methane cost price based on the marginal cost of feedstock and added costs from efficiency, depreciation, capital (CAPEX) and downstream processing.

	CO_2	+	$4 H_2$	$\longrightarrow$	CH_4	+	$2 H_2O$
Mass balance	2750 kg		500 kg		1000 kg		2250 kg
CH_4 marginal cost	$\frac{2750}{1000}$ t × 50 €/t	+	$\frac{500}{1000}$ t × 2200 €/t	=	1238 €/t		
Efficiency			1238 × 0.10	=	248 €/t		
Depreciation			1238 × 0.15	=	186 €/t		
CAPEX			1238 × 0.20	=	248 €/t		
Downstream processing			1238 × 0.10	=	124 €/t	+	
Total CH_4 cost					2042 €/t		

Based on the calculation of the total methane cost price, the marginal cost price of €1238 per ton increases with 65 % to a total cost price of €2042 per ton. However, this is the case when using and electricity price of €40 per MWh a CO_2 price of €50 per ton. Lower electricity and CO_2 prices will reduce the total cost price. Therefore, the total cost price is calculated for a range of electricity and CO_2 prices, to see whether there is a range for the feedstock prices at which methane will be economically feasible.

Figure B.1 shows the methane cost price for different CO_2 prices as a function of electricity price. The cost price is compared to the low market price of 30 €/ton for the Middle East and the high price for Europe of 165 €/ton. These market prices are selected as an upper and lower value for the methane market price.

What can be seen when looking at Figure B.1 is that for all the lines representing the different CO_2 prices, the low Middle East market price, represented by the green dashed line, is lower than he methane total cost price. This means that there is no combination of electricity price and CO_2 price at which it would be feasible to produce methane in the Middle East. The only case in which a profit can be made from methane production by means of hydrogenation is when the CO_2 price would drop any further, i.e. when the CO_2 would be available for free. For the European methane market price shown by the black dashed line there are some cases that will result in the economic feasibility of methane. These are represented by the line sections under

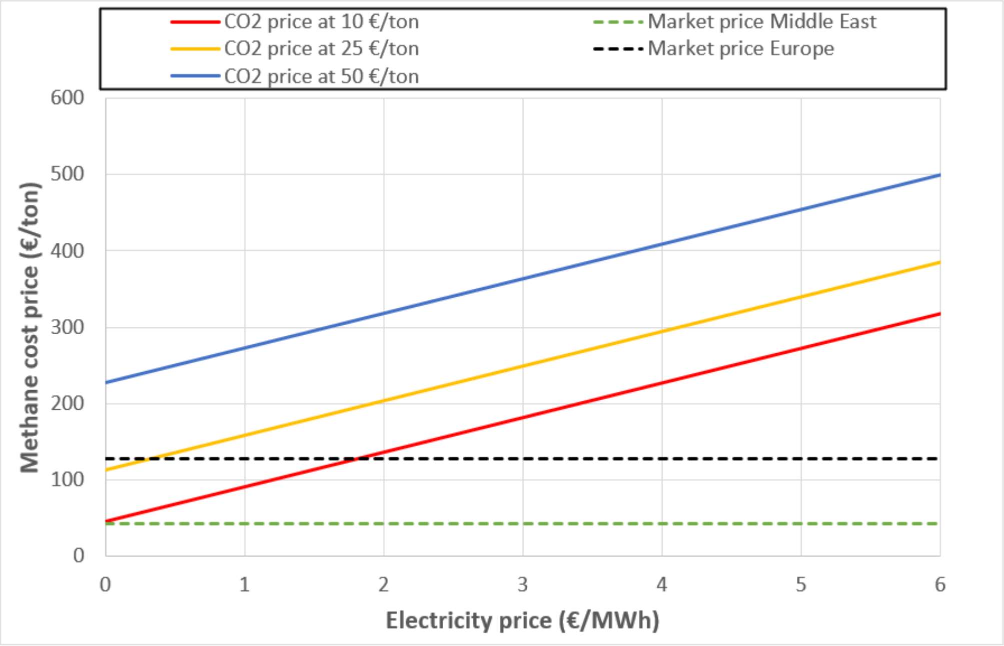

Figure B.1: Methane cost price in €/ton as a function of the electricity price in €/MWh for different CO_2 prices given in €/ton. The non-dashed lines represent the methane cost price at different CO_2 prices for 10, 25 and 50 €/ton, while the dashed lines represents the low and high market price for the Middle East and Europe respectively

the black dashed line, where the market price is higher than the methane cost price. However, these sections only occur at very low electricity below 2 €/MWh for the cases where the CO_2 price is 10 or 25 €/ton. And then still the profit would be low.

Conclusions that can be drawn based on the analysis of the methanol market price for the hydrogenation of CO_2, with H_2 supplied by water electrolysis is performed are:

- The economic feasibility for the production of methane through CO_2 hydrogenation is dependant on the location where it is produced as market prices vary globally.
- Secondly in the cases that methane is a feasible production route, the window of feedstock prices, which are the electricity and CO_2 price, is very small. This window is shown by the line sections in Figure B.1 that lie below the black dashed lines. The window lies somewhere between an electricity price of 0-2 €/MWh and CO_2 price of 0-25 €/ton. Such low electricity prices hardly exist so one can conclude that methanation in general is never a feasible production route. The exception being when feedstock costs are available for free