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# Renewable CO<sub>2</sub> Recycling and Synthetic Methanol Production Using Solar Energy

Master's thesis in Chemical Engineering and Biotechnology

Supervisor: Professor Magne Hillestad

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# Abstract

The demand for energy in the world is increasing, and with that the need for new energy sources. A problem using fossil fuels as an energy source, is the huge amount of CO<sub>2</sub> that comes with it. Consequently, the demand for renewable energy sources is increasing as well.

One possible source of renewable energy is to produce methanol from CO<sub>2</sub> extracted from seawater. The extracted CO<sub>2</sub> can be converted into CO using the reverse water gas shift (RWGS), which in turn can be converted into methanol by hydrogenation. With floats of solar panels, the energy received to produce the methanol can be obtained.

In this thesis, two different designs of methanol production are compared, one where the CO<sub>2</sub> is pre-processed in a RWGS reactor, and one where a RWGS reactor is not present. The purpose of this comparison is to determine if the technology is feasible, if the design with the RWGS reactor leads to an increase in production of methanol, and in that case, how much the production increases.

The two designs are modeled in Aspen HYSYS V9 (Aspen Technology, Inc.), and optimized with respect to hydrogen/carbon ratio, temperature and pressure. After optimization, a carbon conversion ratio of 98 % and 96 % was obtained, for the RWGS reactor design and the design without the RWGS reactor respectively. The purity of the product stream was found to be 99 % for the design with the RWGS reactor and 96 % for the design without the RWGS reactor. The feasibility for this technology looks promising. However, the cost associated with production are high compared to traditional production, and further investigation into the kinetics and cost estimation is therefore needed.

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# Sammendrag

Verdens energibehov øker, og med det behovet for nye energikilder. Et problem med fossilt brensel som energikilde er den store mengden CO<sub>2</sub> som dette medfører. En konsekvens av dette er at verdens behov for fornybare energikilder øker.

En mulig kilde til fornybar energi er å produsere metanol fra CO<sub>2</sub> ekstrahert fra sjøvann. CO<sub>2</sub> kan ved å bruke revers vann-gass skift reaksjonen produsere CO som videre kan bli omgjort til metanol ved hjelp av hydrogenering. Med flåter av solcellepanel kan energien som trengs skaffes.

Målet med denne avhandlingen er å sammenligne to forskjellige design for metanolproduksjon fra CO<sub>2</sub>, en hvor føden blir preprosessert i en revers vann-gass skift reaktor, og en hvor den ikke blir det. Målet med denne sammenligningen er å se om teknologien er gjennomførbar, og om det preprosesserte designet produserer mer metanol, og i så fall hvor mye.

De to designene har blitt modellert i Aspen HYSYS V9 (Aspen Technology, Inc.), og optimalisert med hensyn på hydrogen/karbon forholdet, temperatur og trykk. Etter optimaliseringen ble en omsetningsgrad av karbon på 98 % funnet i designet med revers vann-gass skift reaktor og på 96 % i designet uten. Renheten til de to produktstrømmene er 99 % metanol for designet med revers vann-gass skift reaktor og 96 % metanol for designet uten. Gjennomførbarheten til teknologien ser veldig bra ut, men kostnadene med produksjonen er høy sammelignet med tradisjonell produksjon, videre forskning på kinetikken og kostanalyse vil derfor være nødvendig.

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# Preface

This master thesis describes my work for my Master of Science degree in Chemical Engineering at the Norwegian University of Science and Technology (NTNU), researcher group of Environmental Engineering and Reactor Technology at the Department of Chemical Engineering (IKP).

I would like to use this opportunity to thank my supervisor Professor Magne Hillestad, for guidance and support with this thesis.

I have written this master thesis alone. The initial Aspen HYSYS (Aspen Technology, Inc.) files was given to me by Professor Magne Hillestad, and edited and optimized by me. All calculations are done by me.

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# Abbreviations

BP MED = Bipolar membrane electro dialysis

PFR = Plug flow reactor

RWGS = Reverse water gas shift

IPCC = Intergovernmental Panel on Climate Change

# Introduction

Worldwide, there is an increasing energy consumption, where the main source of energy is fossil fuels. A consequence of a higher consumption of fossil fuels is an increase in release of  $\text{CO}_2$ , showed to have a negative effect on the climate [1]. The Intergovernmental Panel on Climate Change (IPCC) stated in 2018 that to reach the goal for the temperature on the globe not to increase with more than  $1.5\text{ }^\circ\text{C}$  there has to be a net  $\text{CO}_2$  emission of zero within 15 years [2]. To substitute the use of fossil fuels, it is therefore important to find new sources of renewable energy.

The use of fossil fuels, like oil and gas, are one of the main causes for  $\text{CO}_2$  emissions, and high amounts of  $\text{CO}_2$  are naturally being stored in the ocean. Extracting  $\text{CO}_2$  in the ocean and turning it into usable compounds is a way of getting renewable hydrocarbon based fuels, as this frees up space in the ocean to take up more  $\text{CO}_2$  from the atmosphere. This will also decrease the need for hydrocarbons from reservoirs, resulting in less  $\text{CO}_2$  released into the atmosphere. Renewable methanol is a hydrocarbon that is a possible successor to fossil fuels, as it has the same properties as methanol from non-renewable sources [3].

Methanol production is usually produced with syngas made from methane extracted from gas fields. By changing the production of methanol to instead use  $\text{CO}_2$  extracted from seawater and hydrogen gas produced from electrolysis, it is possible to make renewable methanol [4]. Using a floating plant reveals the op-

portunity of using large areas that previously has been unusable for production of methanol. Utilizing the large area for floats of solar panels makes it possible to get the production of methanol 100 % renewable.

## 1.1 Objective

The objective of this thesis is to evaluate two different process structures designs for methanol production with CO<sub>2</sub> from seawater, one where the feed is pre-processed in a reverse water gas shift reactor before entering the methanol reactor, and one where the methanol reactor feed is not pre-processed. The goal is to model and optimize the two designs using Aspen HYSYS (Aspen Technology, Inc.), and look at the feasibility of the technology. Another objective is to make and evaluate a cost estimation of the difference between the two process structures, to look at the profitability.

## 1.2 Declaration of Contribution

The two process structures for this thesis were proposed by Professor Magne Hillestad. The initial Aspen HYSYS (Aspen Technology, Inc.) files were built by Professor Hillestad. All the other work reported in this master thesis, is done by me.

My main contributions are:

- Editing and optimization of the files from Aspen HYSYS V9 (Aspen Technology, Inc.).
- Implementation of a heat integration network.
- Sizing and cost estimation of equipment.
- Compare process configurations.
- Look at the feasibility of the process technology.

# Methanol Production

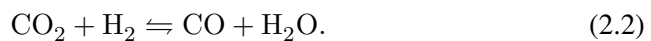
In this chapter, a more detailed description of the methanol production process is presented.

## 2.1 Methanol Synthesis

Synthesis of methanol is usually produced from methane turned into synthesis gas [5], but can also be produced directly by hydrogenation of carbon monoxide [6], as shown in Equation (2.1)

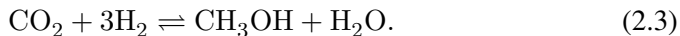


However, it is possible to produce methanol from  $\text{CO}_2$  by utilizing the reverse water gas shift reaction, where CO and  $\text{H}_2\text{O}$  can be produced [7], as shown in Equation (2.2)



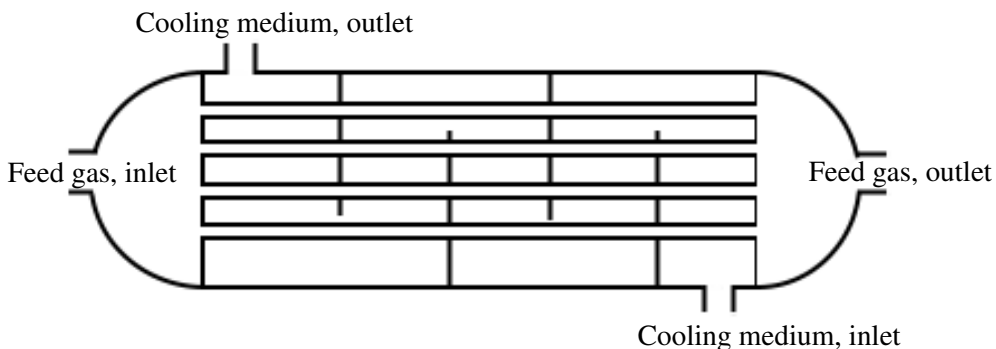
By combining Equation (2.1) and Equation (2.2), the total reaction for the methanol

synthesis becomes



Both Equation (2.1) and Equation (2.3) are exothermic reactions that prefer low temperatures and high pressures.

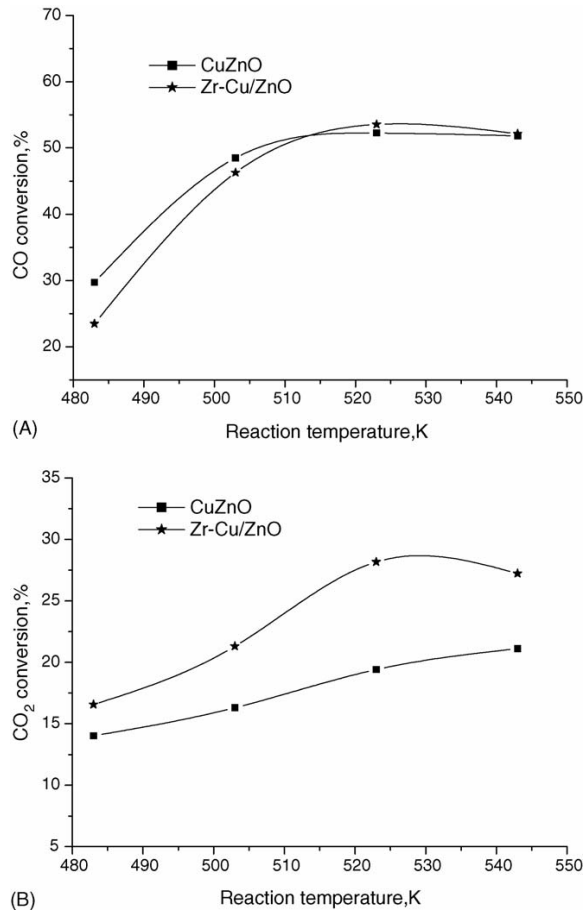
The production of methanol is produced using a plug flow reactor (PFR) with multiple pipes and cooling around each pipe as illustrated in Figure 2.1.



**Figure 2.1:** An illustration of a plug flow reactor (PFR) configured as a shell and tube heat exchanger.

The advantage with using a PFR configured as a shell and tube heat exchanger, is the possibility to have good heat transfer, to or away from the inner tubes, where the reaction is taking place, so that the temperature can be as constant as possible [8]. This is an advantage when the reaction has a small temperature area as the temperature could be held at the optimal temperature of the reaction, to get a better yield.

The catalyst used in traditional methanol production is Cu–Zn–Al oxide catalyst [9]. This catalyst works best in CO rich feed. For a feed with higher concentration of  $\text{CO}_2$  this catalyst does not perform as well [10]. A CuZnO doped with  $\text{ZrO}_2$  would work much better when the concentration of  $\text{CO}_2$  is higher [9], as demonstrated in Figure 2.2.



**Figure 2.2:** Conversion (%) of CO and CO<sub>2</sub> using a CuZnO catalyst and a Zr–Cu/ZnO catalyst [9].

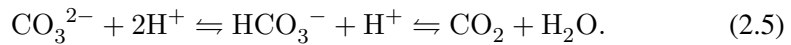
## 2.2 Hydrogen Production

Hydrogen gas is an important part of the production of methanol as it is included in both the hydrogenation of CO and the RWGS reaction, as shown in Equation (2.2) and Equation (2.1). This can be produced by electrolysis of water [11]. The reaction of splitting water can be written as



## 2.3 Feed Extraction

CO<sub>2</sub> can be extracted from seawater using an Eisaman bipolar membrane electro-dialysis (BPMED) cell [12]. This cell allows for a flow rate of CO<sub>2</sub> of approximately 5 L/min. This cell works by converting CO<sub>3</sub><sup>2-</sup> in an acidic environment, from the seawater, into HCO<sub>3</sub><sup>-</sup>, and further into CO<sub>2</sub> and H<sub>2</sub>O [12]. The reaction is shown in Equation (2.5),



Using the CO<sub>2</sub>, captured from the Eisaman BPMED cell, with H<sub>2</sub> extracted from seawater using electrolysis, as described in Equation 2.4, all the necessary ingredients to produce methanol is fulfilled.

## 2.4 Reversed Water Gas Shift Reactor

By pre-processing the CO<sub>2</sub> feed in a RWGS reactor, it may be possible to increase the production of methanol. To increase the rate of the RWGS reaction, a catalyst could be applied. The choice of catalyst in a RWGS reactor depends on the desired temperature and yield. Both the ZnO catalyst and the ZnO/AlO<sub>3</sub> catalyst has a conversion rate approximately at equilibrium for a temperature of 650 °C, as shown in Figure 2.3. However, the ZnO catalyst has shown low stability and deactivates at 600 °C, ZnO/AlO<sub>3</sub> is therefore a better choice for reactors using temperatures over 600 °C [13].



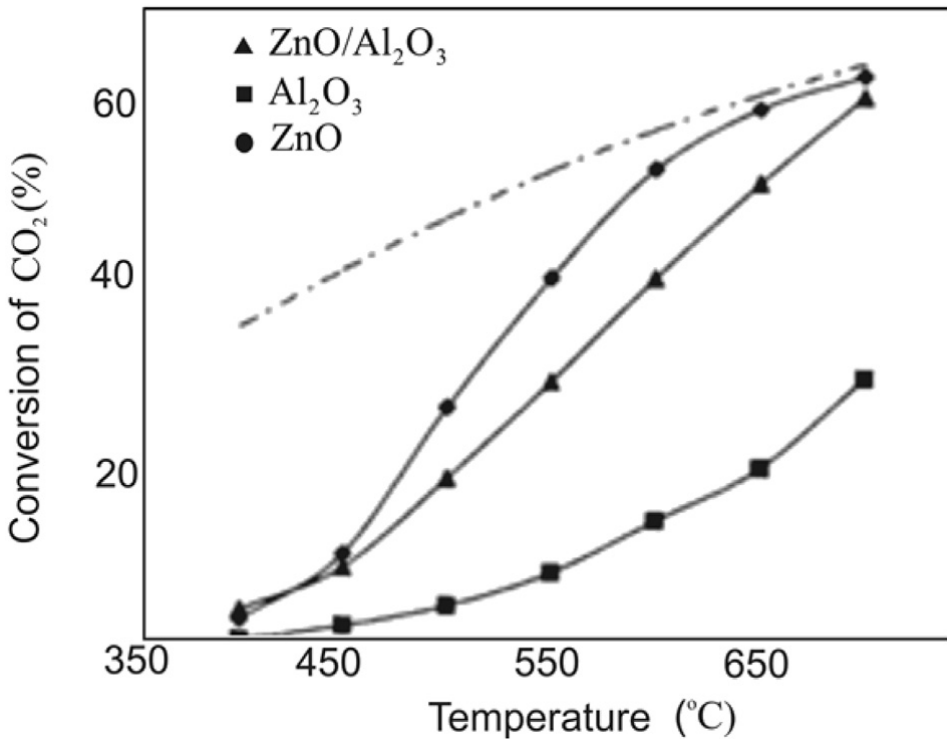


Figure 2.3: Conversion of CO<sub>2</sub> using different catalyst [13, 14].

## 2.5 Heat Integration

To improve the energy efficiency of a process, a heat integration system can be implemented. In this system, warm streams that need to be cooled are paired up with cold streams that are to be heated, thus making use of energy that would otherwise go to waste. To make the most out of the possible energy saving, a heat integration system could be designed.

The most common method of designing a heat integration network is by "pinch-analysis". In the "pinch-analysis" there is a minimum temperature difference,  $\Delta T_{min}$ , between the hot and the cold stream. This temperature is usually set to at least 10 °C. It is possible to find the minimum temperature difference in the network, also known as the pinch either by doing it graphically, using the composite curve, or by using "The Problem Table Method" [15].

The problem table method is given below:

1. The temperature of the streams are shifted to  $T^*$ , by adding  $\Delta T/2$  to the cold streams, and subtracting  $\Delta T/2$  from the hot streams.
2. Arrange the streams in temperature intervals, each interval only given once.
3. Calculate the enthalpy for each interval:

$$\Delta H_i = (\Sigma C p_c - \Sigma C p_h) \Delta T_i \quad (2.6)$$

where  $\Delta H_i$  is the energy received in interval  $i$ ,  $Cp$  is the heat capacities for the cold and hot streams and  $\Delta T_i$  is the temperature difference in interval  $i$ .

4. Cascade the heat surplus from one interval down to the next.
5. Apply the smallest amount of heating needed at the top to eliminate negative values.

The heat recovery pinch occurs where the heat flow in the cascade is zero. The heat integration network should be designed from the pinch. A criteria for the heat capacities is that [15]

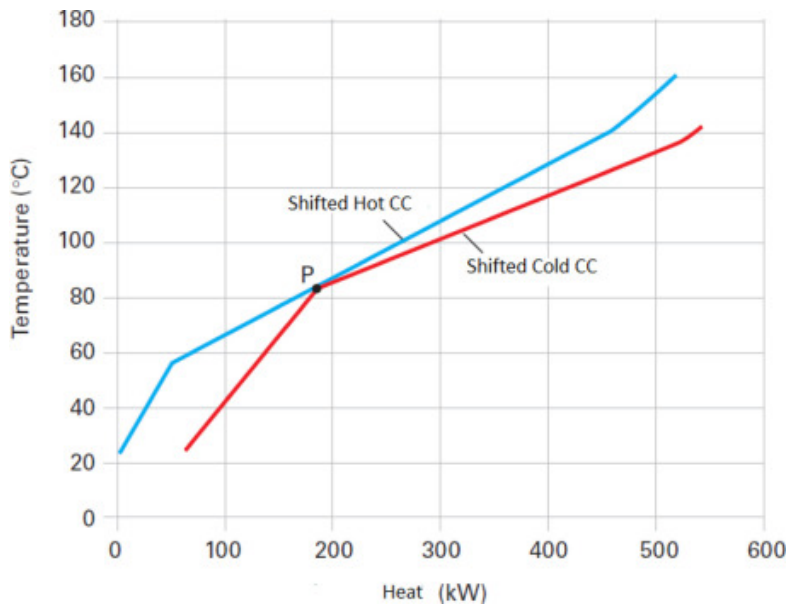
$$\text{Above pinch: } C p_h \geq C p_c$$

$$\text{Below pinch: } C p_h \leq C p_c.$$

The composite curve is made by plotting the shifted temperature of the streams in the heat integration network as a function of enthalpy (H), see Figure 2.4. The minimum temperature difference of the network can be found as a point on the composite curve, and is known as the heat recovery pinch. This separates the streams into two different systems, one above the pinch, and one below [15].

There is a possibility that the heat recovery network does not have a heat recovery pinch. In that case, known as a threshold problem, it is only necessary with either a hot or a cold utility. When designing a heat integration network of a threshold problem the design is usually started at the most constrained part [15].

For processes with multiple streams, there are several possible designs for the heat recovery network. On a floating plant, there is reduced space, so the design of the heat recovery network should be as compact as possible, which limits the number



**Figure 2.4:** Example of a shifted hot composite curve and a shifted cold composite curve, where the pinch is marked with P [16].

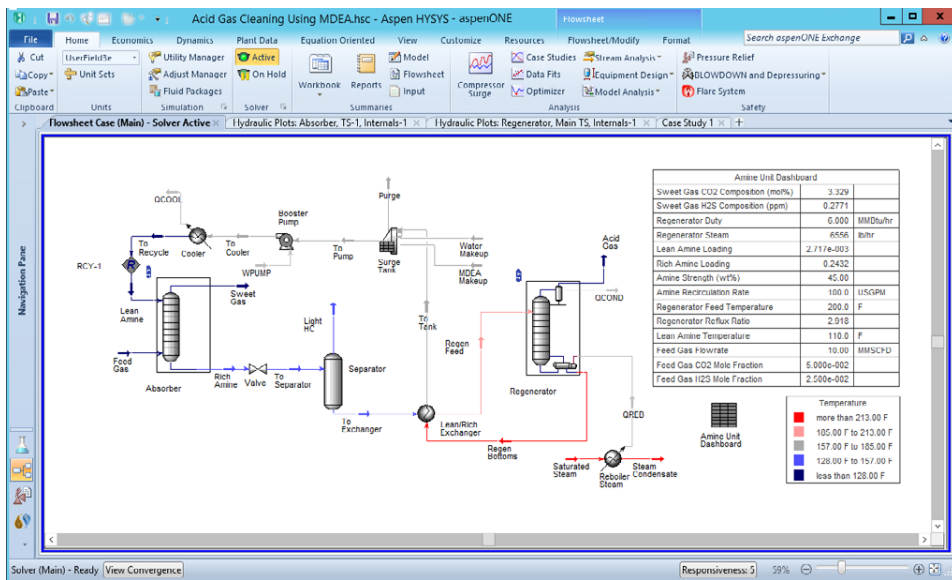
of possible designs. Reducing space can be achieved by having large temperature differences, so the driving forces is as large as possible, resulting in needing less heat transfer area.

For onshore plants, air-cooling is often used due to water limitations. However, on a floating plant this is not as important, as there is a surplus of seawater that can be used for cooling the system. This is an advantage as water has higher heat capacity than air making it a better heat conductor.

There are two possibilities for water-cooling for the plant. One way is to use seawater directly in the exchangers to cool the hot stream. Another way is to use a fresh water cycle, where fresh water is exchanged with the hot stream and is cooled by the seawater. The downside of using this method is that it needs an extra exchanger between the seawater and the fresh water. The use of seawater in the cooling cycle has some disadvantages as well, as the salt in the water increases the corrosion on the equipment.

## 2.6 HYSYS

Aspen HYSYS(Aspen Technology, Inc.) is a process modeling tool for designing and performance improving of oil and gas processes. Aspen HYSYS (Aspen Technology, Inc.) has an environment in which it is possible to design processes and size equipment. The program has a large database of thermodynamic data of compounds it uses to calculate the physical properties of the process. A library of unit operations models is also added, such as distillation columns and reactors [17]. An example of the user interface is given in Figure 2.5

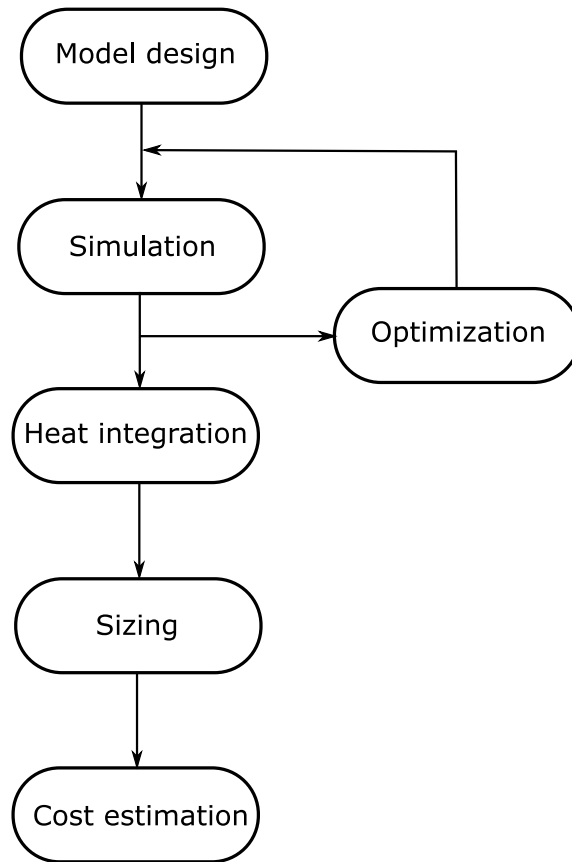


**Figure 2.5:** Example of the user interface in Aspen HYSYS V9 (Aspen Technology, Inc.) [18].

# Chapter 3

## Method

This chapter contains the method used to arrive at the results given in Chapter 5. The flow chart in Figure 3.1 shows an overview of the method used in the thesis. Starting by finishing the HYSYS design and simulation, for then to optimize the input parameters for the simulation, heat integration, sizing, and finally create a cost estimation of the plant.



**Figure 3.1:** A flow chart outlining the workflow of this thesis.

### 3.1 HYSYS

This section presents information about how the simulation of the two designs was performed. The simulation flow sheets can be found in Appendix A. A flow sheet of the design, where the total reaction is taking place in the methanol reactor, is shown in Figure 3.2, and a flow sheet with a reverse water gas shift reactor to pre-process the feed, is shown in Figure 3.3.

The simulations were performed using Aspen HYSYS V9 (Aspen Technology, Inc.) V9. To get the equation of state, the property package used was Peng-Robinson.

Both simulations start out with a stream of pure  $\text{CO}_2$ , and a stream of  $\text{H}_2$ . The

CO<sub>2</sub> stream is pressurized, and mixed with the H<sub>2</sub> stream, and a recycle stream. After the mixing, the stream is further pressurized over several steps, with cooling between each step. In the simulation with the reverse water gas shift reactor, the gas is heated after the last compression, and is fed into an equilibrium reactor, where the RWGS reaction is taking place. The stream is then cooled to 40 °C and water is separated out, and the stream is reheated. For both simulations the stream is then mixed with another recycle stream, before it is preheated with the out stream of the methanol reactor. The stream then enters the PFR reactor, producing methanol.

The Aspen HYSYS V9 (Aspen Technology, Inc.) files were provided by Professor Magne Hillestad, and edited and optimized by me. In the RWGS model, a separator to extract the water after the RWGS reactor was included.

To find the optimal ratio between CO<sub>2</sub> and H<sub>2</sub>, a case study was used. The case study looked at the H<sub>2</sub>/CO<sub>2</sub> ratio in the range 1.5 to 4.6. This was done by making Aspen HYSYS V9 (Aspen Technology, Inc.) hold the CO<sub>2</sub> input constant and changing the H<sub>2</sub> stream. The optimal ratio was then found by looking at the product stream of methanol.

Similarly as for the H<sub>2</sub>/CO<sub>2</sub> ratio, the optimal temperature and the optimal pressure were found using case studies. The temperature case span from 200 °C to 600 °C. The pressure case span from 50 bar to 100 bar. The goal of the case studies was to maximizing the production of methanol.

The inlet stream of CO<sub>2</sub> was set to 56 kmole/h, and from the optimization of the H<sub>2</sub>/CO<sub>2</sub> ratio an inlet stream of H<sub>2</sub> was set to 168 kmole/h. The mole fraction of CO<sub>2</sub> was set to 1 as the membrane extracting the CO<sub>2</sub> only allows CO<sub>2</sub> to pass. The mole fraction of H<sub>2</sub> in the hydrogen stream was set to 0.9975 as some water and methane passes through the extraction process. The input parameters for the simulation are given in Table 3.1 and Table 3.2.

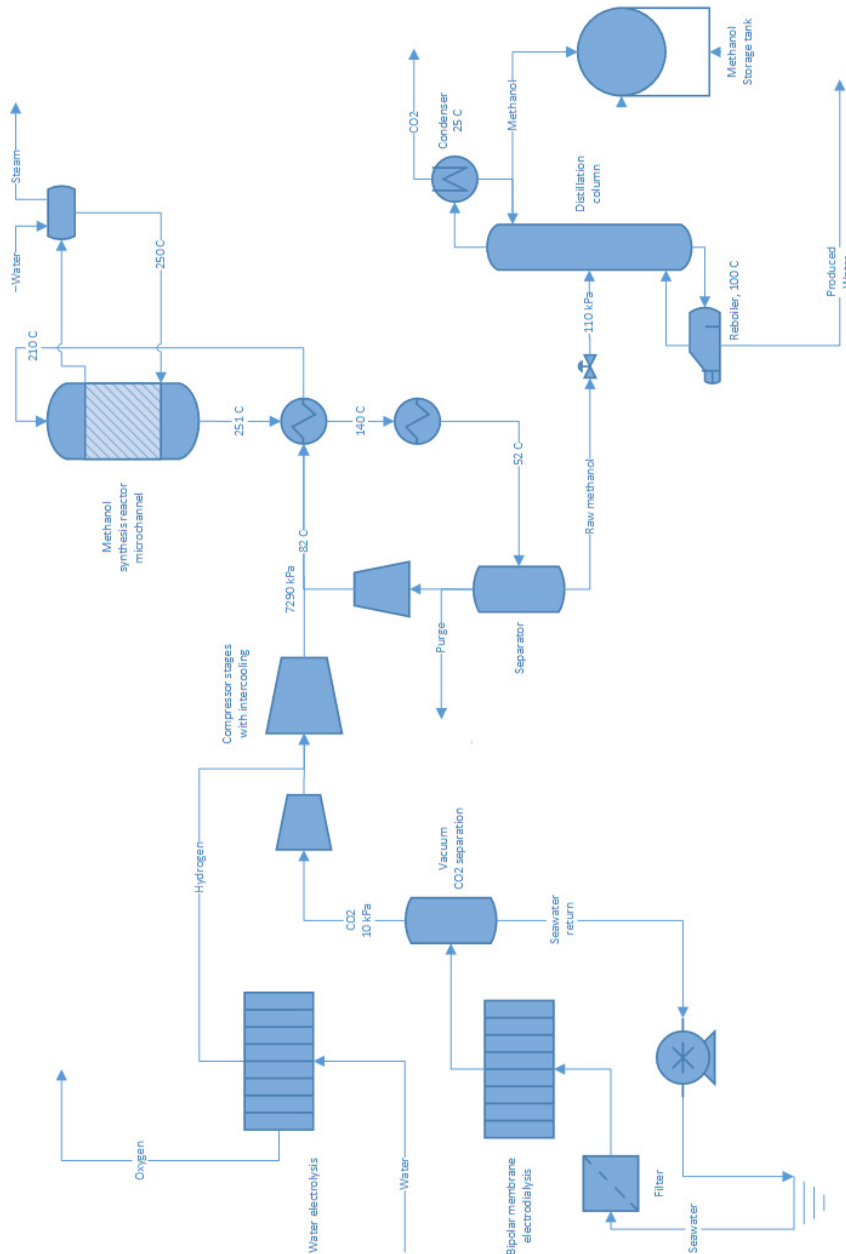
**Table 3.1:** Mole fractions of inlet streams.

Component	Mole fraction
<b>Hydrogen stream</b>	
H <sub>2</sub>	0.9975
H <sub>2</sub> O	0.0012
CH <sub>4</sub>	0.0012
<b>CO<sub>2</sub> stream</b>	
CO <sub>2</sub>	1

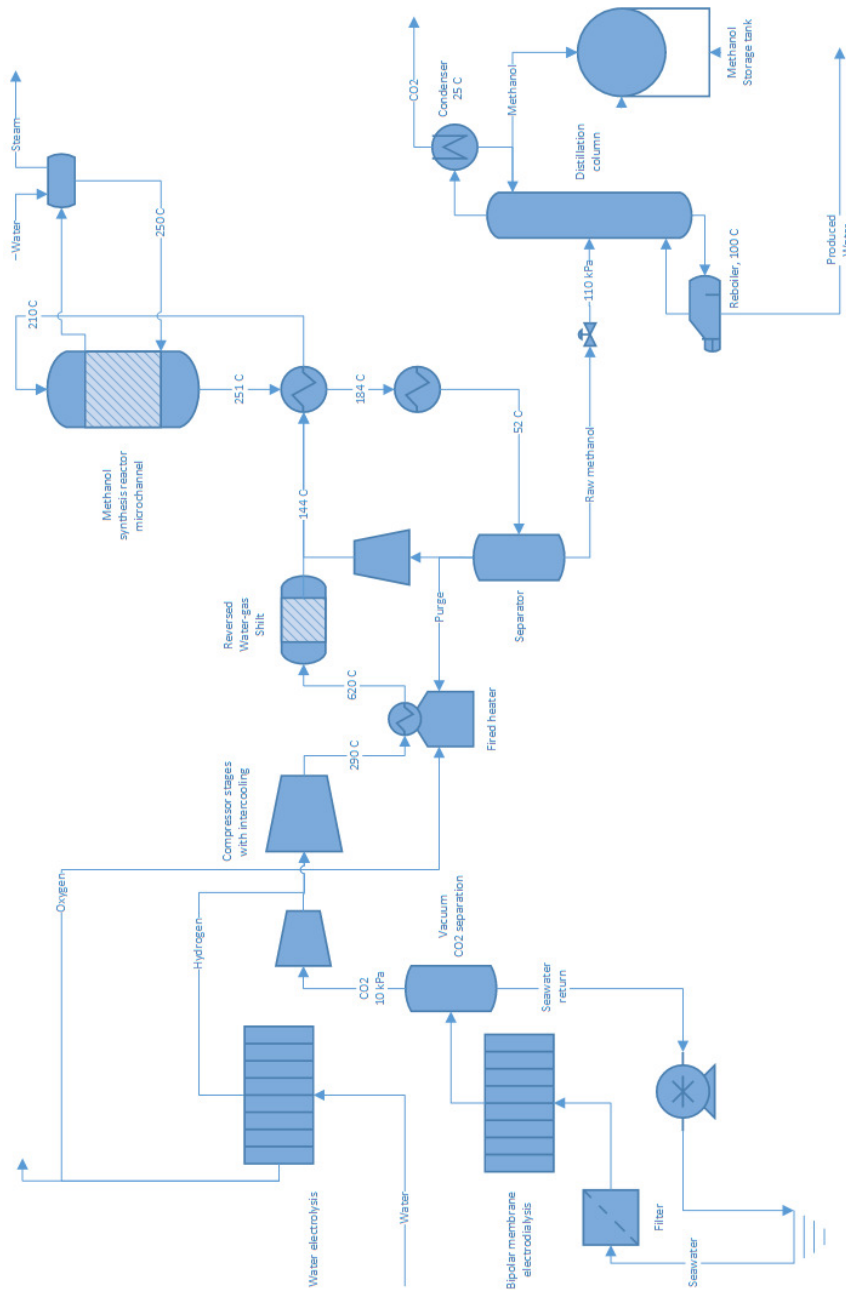
**Table 3.2:** Inputs for the design

Parameter	Value
Hydrogen steam [kmole/h]	168
CO <sub>2</sub> stream [kmole/h]	56
Inlet temperature [°C]	50
Inlet RWGS reactor [°C]	620
Inlet methanol reactor [°C]	210





**Figure 3.2:** A flow sheet of the methanol plant without a reverse water gas shift reactor. Received from Professor Magne Hillestad.



**Figure 3.3:** A flow sheet of the methanol plant with a reverse water gas shift reactor. Received from Professor Magne Hillestad.

## 3.2 Heat Integration

For the process structure including the RWGS reactor there is a possibility to design a heat integration network to reduce the energy needed to operate the plant. Several streams could be included in the network, however, there are more streams that needs cooling than streams that needs heating. The hot streams chosen for the heat integration network are:

1. The outlet of the methanol PFR.
2. The outlet of the RWGS reactor.

The cold streams chosen are:

3. The outlet of the water separator.
4. The inlet to the methanol PFR.
5. The inlet to the RWGS reactor.

The pinch of this network was found using the composite curve method. The hot and cold streams were divided into temperature intervals with the corresponding enthalpy intervals. These intervals were then plotted into MATLAB 2017a (The MathWorks, Inc.) and adjusted so that the minimum temperature difference was 10 °C.

For the process structure without the RWGS reactor there is not designed a heat integration network due to the fact that there is no need as there is no streams that is heated.

## 3.3 Sizing

In this section, the methods for sizing of the main equipment used will be listed. All equipment is assumed made of stainless steel. All calculations are done using SI units.

### 3.3.1 Pressure Vessel

Pressure vessels are used in calculations of separators, reactors, and distillation columns. For a pressure vessel to be able to hold a specific pressure it is important that the thickness of the walls is large enough. The equation used to calculate the wall thickness needed is given in Equation (3.1) [19],

$$t = \frac{P_i D_i}{2SE - 1.2P_i}, \quad (3.1)$$

where  $t$  is the thickness of the walls,  $P_i$  is the pressure inside the vessel,  $D_i$  is the diameter of the vessel,  $S$  is the maximum allowable stress, and  $E$  is the welded-joint efficiency.

If the thickness of the walls is known, the shell mass of the pressure vessel is calculated as shown in Equation (3.2) [19]

$$\text{Shell mass} = \pi D_i L_i t \rho, \quad (3.2)$$

where  $L_i$  is the length or height of the vessel and  $\rho$  is the metal density. Since stainless steel is assumed to be used in all equipment a metal density of 8000 kg/m<sup>3</sup> was used. [19].

### 3.3.2 Separator

To be able to size the separators, the settling velocity of droplets needs to be found. This is estimated using Equation (3.3) [19]

$$u_t = 0.07 \sqrt{\frac{\rho_L - \rho_g}{\rho_g}}, \quad (3.3)$$

where  $u_t$  is the settling velocity,  $\rho_L$  is the liquid density, and  $\rho_g$  is the gas density.

The minimum diameter of the separator is then calculated using Equation (3.4) [19]

$$D_v = \sqrt{\frac{4V_g}{\pi u_t}}, \quad (3.4)$$

where  $D_v$  is the minimum vessel diameter and  $V_g$  is the gas volumetric flow rate.

The height of the separator is calculated by having a height of  $D_v$  over the inlet, and a height of  $0.5D_v$  below the inlet, but no less than 1 m over, and 0.6 m below the inlet. There should also be added minimum 0.4 m if a demister pad is used, and the height of the liquid in the separator, which depends on the holdup time in the separator, typically 10 minutes. The height of the separator is then calculated using Equation (3.5)

$$h = 0.4 + \max[1, D_v] + \max[0.6, 0.5D_v] + h_l, \quad (3.5)$$

where  $h$  is the height of the separator, and  $h_l$  is the height of the liquid in the separator [15].

### 3.3.3 Distillation Column

The dimensions of the distillation column are calculated using Aspen HYSYS V9 (Aspen Technology, Inc.), and from that the mass of the distillation column is calculated as a pressure vessel, Equation (3.2).

## 3.4 Cost Estimation

To estimate the design cost of equipment, equation (3.6) was used

$$C_e = a + bS^n, \quad (3.6)$$

where  $C_e$  is the purchased equipment cost on a US Gulf Coast basis, Jan. 2007,  $a$  and  $b$  are cost constants.  $S$  is a size parameter, and  $n$  is an exponent for different kind of equipment [19].

Numbers for the size parameter and the constants for each type of equipment are given in Table 3.3.

**Table 3.3:** Data for estimating purchased equipment cost for plant equipment. [19]

<b>Equipment</b>	<b>Unit for S</b>	<b>S<sub>lower</sub></b>	<b>S<sub>upper</sub></b>	<b>a</b>	<b>b</b>	<b>n</b>
<b>Compressors</b>						
Centrifugal	Driver power [kW]	75	30,000	490,000	16,800	0.6
<b>Exchangers</b>						
U-tube shell and tube	Area [m <sup>2</sup> ]	10	1000	20,000	46	1.2
<b>Pressure vessel</b>						
Vertical,304ss	Shell mass [kg]	120	250,000	15,000	68	0.85
<b>Trays</b>						
Sieve tray (per tray)	Diameter [m]	0.5	5.0	110	380	1.8

Since Equation (3.6) gives the US Gulf Coast basis for January 2007, this has to be converted to 2018 prices. To account for cost escalation Equation (3.7) is used

$$\text{Cost year A} = \text{Cost year B} \cdot \frac{\text{Cost index year A}}{\text{Cost index year B}}, \quad (3.7)$$

where "Cost year B" is the calculated price for a given year, "Cost index year B" is the cost index for the same year, "Cost index year A" and "Cost year A" is respectively the cost index and the cost for the year that are to be calculated [19].

# Chapter 4

## Literature Study

Production of methanol usually consist of three parts, synthesis gas production, methanol production, and methanol distillation. The commercial production of methanol was first implemented in 1923, and has changed over the years [20]. The drive of these changes are economical either by lowering the cost of production, or other cost like taxes. Methanol is most commonly produced from synthesis gas, which is a mix of CO, CO<sub>2</sub>, and H<sub>2</sub>. The method implemented in 1923 was a high pressure process, using pressures between 240-300 bar and temperatures around 300-450 °C [20]. In the 60's, production was changed to low pressure, 50-100 atm, and temperature at 200-300 °C as a result of better catalyst [21]. Today there are two processes dominating the market, the ICI process, and the Lurgi process. The ICI process uses multibed reactors with feed-gas quench cooling. The Lurgi process uses multitubular reactors with internal cooling. [22]

The common way of producing synthesis gas is by reforming natural gas using a steam reformer, and an autothermal reformer [23]. The problem with this is the increasing focus on renewable energy. However, with the use of the reverse water gas shift reaction there is a way of taking captured CO<sub>2</sub> and turning this into CO and thereby making the production of methanol renewable. There are several articles looking into the profitability of making methanol from captured CO<sub>2</sub>. This will in turn result in a cut in operating costs as a consequence of CO<sub>2</sub>-taxation [4]. Szima et al. [24] stated that to make methanol from captured CO<sub>2</sub> profitable today

the price of methanol has to increase to about double the price, or the production cost has to be reduced .

There are several ways of producing methanol from  $\text{CO}_2$ , two of which was compared by Anicic et al. in 2014 [14]. This article compared the methanol process with, and without a reverse water gas shift reactor to make synthesis gas before the methanol reactor. Anicic et al. developed two designs similar to the designs in this thesis, one with a RWGS reactor, and one without a RWGS reactor. The design with the RWGS reactor included a separator to remove the water after the RWGS reactor, and a methanol reactor, before distillation of the product. The design without the RWGS consist of two methanol reactors with a flash separator to extract the product [14]. Both designs start out with a stream of  $\text{CO}_2$  of 44,000 kg/h, and a stream of  $\text{H}_2$  of approximately 5,000 kg/h, a little under in the design with the RWGS reactor, and a litter over in the design without. The designs get a mass flow of methanol of 25,270 kg/h and 28,714 kg/h for the design with the RWGS reactor and the design without the RWGS reactor respectively. The article concludes that the design without the RWGS reactor has a slightly higher economical and energetic efficiency, but they say this difference is fairly insignificant. [14].



# Chapter 5

## Results

In this chapter the different results from the methods described in Chapter 3 are presented.

### 5.1 Optimization

The optimized parameters found with the case studies in Aspen HYSYS V9 (Aspen Technology, Inc.) are given in Table 5.1. The optimal ratio between CO<sub>2</sub> and H<sub>2</sub> was found to be 3, the optimal temperature was found to be 250 °C, and the optimal pressure was found to be 73 bar.

**Table 5.1:** Optimized parameters with case studies in Aspen HYSYS V9 (Aspen Technology, Inc.).

Parameter	Optimal solution
H <sub>2</sub> /CO <sub>2</sub>	3
MathaReactor temperature	250 °C
Pressure	73 bar

## 5.2 Simulation

Table 5.2 shows the methanol stream for both design as well as the conversion ratio of CO<sub>2</sub> and the purity of the product stream. Both designs have a high conversion ratio and purity. The design with the RWGS has a conversion ratio of 98 %, and a purity of 99 %. The design without the RWGS reactor has a conversion ratio of 96 % and a purity of 96 %. The product stream is higher in the design without pre-processing, however, the amount of pure methanol produced is higher in the pre-processed design.

**Table 5.2:** Product stream, conversion ratio of CO<sub>2</sub> to methanol, and the purity of the product stream.

Design	With RWGS	Without RWGS
Product flow [kmole/h]	55.69	57.05
Carbon conversion	0.98	0.96
Purity	0.99	0.96
Energy consumption [kW]	5,537	7,775
Pure Methanol [kg/h]	1,766.7	1,729.3

## 5.3 Heat Integration

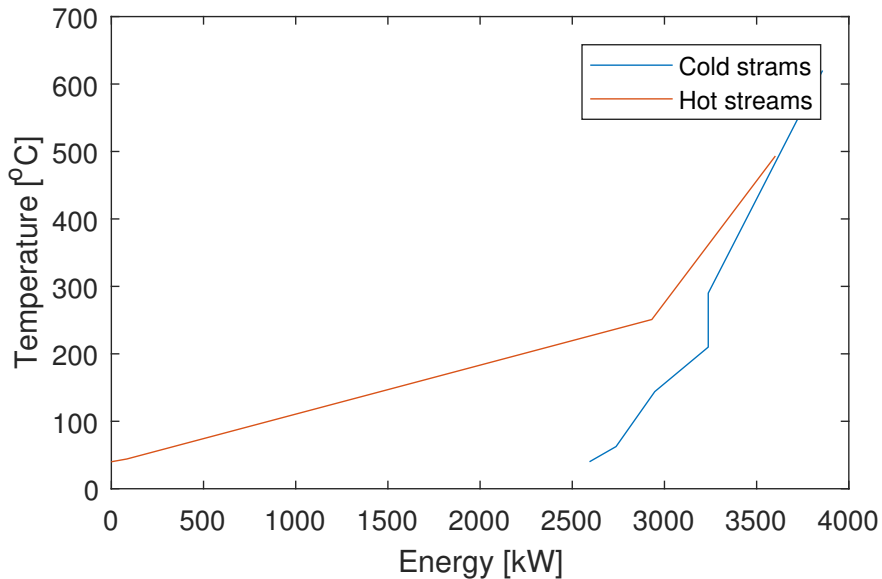
An overview of the temperatures and heat flow of the streams used in the heat integration network for the RWGS design are shown in Table 5.3.

**Table 5.3:** Overview of the streams used in the heat integration.

Stream number	Temp in [°C]	Temp out [°C]	Heat load [kW]
1	205.9	44.1	2,803
2	493.3	40	1,252
3	40	144	180
4	62.53	210	1,414
5	290	620	720

With the use of the composite curve for the process, the pinch of the process was determined to be 488.3 °C, which corresponds to the maximum temperature of the hot streams, as shown in Figure 5.1. Following, the problem can be looked at as a

threshold problem with some additional heating at the end of the cold streams, and some cooling at the end of the hot streams. The final design is illustrated in Figure 5.2



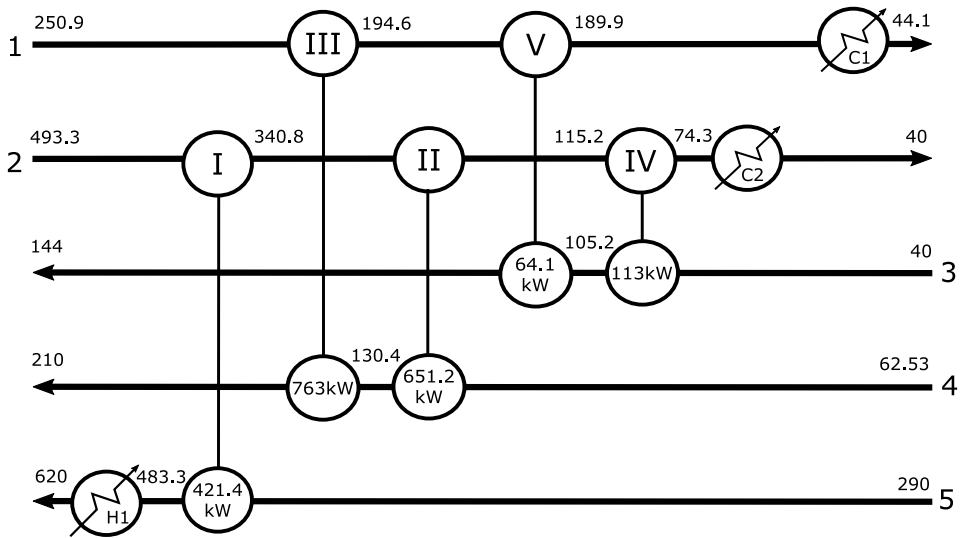
**Figure 5.1:** The Composite Curves for the hot and cold streams included in the heat integration network for design with RWGS reaction.

### Heat Exchanger I

The outlet of the reverse water gas shift reactor (stream 2) is used to preheat the inlet to the same reactor (stream 5). Stream 2 was connected to stream 5, as stream 2 was the only stream hot enough to heat stream 5. The heat transfer is enough to preheat stream 5 up to the pinch, however, some additional heating is needed to heat stream 5 to the desired temperature.

### Heat Exchanger II

After Heat exchanger I, stream 2 still has a lot of energy left and is used to partially preheat the inlet to the methanol PFR (stream 4). The amount of energy used is just enough so that the rest of stream 2 could be used in heat exchanger IV.



**Figure 5.2:** Proposed heat integration network for the design with RWGS reaction, with the effects of the different heat exchangers, and the temperatures in and out of the exchangers, in °C. Stream 5 is heated by stream 2, stream 3 and 4 is heated by both stream 1 and 2. Stream 5 has an extra heater, stream 1 and 2 have an extra cooler.

### Heat Exchanger III

The outlet of the methanol PFR (stream 1) is used to preheat stream 4 up to the desired temperature of 230 °C.

### Heat Exchanger IV

The rest of stream 2 is used to heat the gaseous phase of the separator after the RWGS reactor, but before mixing in the recycle stream (stream 3). The desired temperature of stream 2 is 40 °C, however, it is not possible to completely cool stream 2 with stream 3, because the inlet temperature of stream 3 is 40 °C.

### Heat Exchanger V

Stream 1 is used to heat the rest of stream 3 up to the desired temperature of 144 °C.

## Additional Cooling and Heating

As no of the other streams are hot enough to heat stream 5 any further, it must be heated separately. Stream 2 has been cooled down to the lowest possible temperature with the heat integration network, 50 °C, but needs some further cooling. As all the energy needed to heat the cold streams are used up, stream 1 needs to be cooled separately.

The other streams in the process also have the need for cooling. These streams are cooled with seawater.

## 5.4 Sizing

Table 5.4 shows the different sizing results for the different equipment. The diameter and height of the separators are calculated using Equation (3.4) and Equation (3.5). The mass of the pressure vessels used for separators, and distillation column is calculated using Equation (3.2). As seen from the diameter of both separators, they are both at the minimum diameter possible. This is the case for both designs, so there is no difference in the size of the separators. Both the diameter and the height of the distillation column are given in Aspen HYSYS V9 (Aspen Technology, Inc.), making them similar for both designs.

**Table 5.4:** Size and weight of the different towers. The sizing apply for both the design with reverse water gas shift reactor, and the design without the extra reactor.

Equipment	Diameter	Height	Mass [kg]
Separator (after methanol reactor)	0.5	2	53.24
Separator (after RWGS reactor)	0.5	2	53.24
Distillation column	1.5	16.5	3,951

## 5.5 Cost Estimation

The cost estimation of the different equipment is presented in Table 5.5 and Table 5.6. The cost of the equipment is calculated using Equation (3.6). The cost of the

methanol reactor (PFR-100) is calculated using Equation (3.6) as if it was a heat exchanger.

The cost of the equipment in the design with the RWGS reactor is more expensive, by approximately 410,000 USD. It is clear from Table 5.5 and Table 5.6 that the compressors constitute a major part of the cost. Since all compressors are present in the two designs, the difference in equipment cost is small.

**Table 5.5:** The price of the different equipment in the design with a reverse water gas shift reactor. PFR-100 is the methanol reactor, K-xxx is the compressors, E-xxx is the heaters and coolers used in Aspen HYSYS V9 (Aspen Technology, Inc.), Hex are the heat exchangers designed using the heat integration network, Cx is the additional cooler from the heat integration network and H1 is the heater from the heat integration network.

Equipment	Price [USGC 2007]
Separator (after methanol reactor)	16,994
Separator (after RWGS reactor)	16,994
Distillation column	119,531
PFR-100	94,692
K-100	1,054,612
K-102	702,690
K-103	702,690
K-104	989,710
K-105	989,710
K-106	1,035,026
E-101	48,626
E-102	20,524
E-103	22,037
E-104	22,078
E-105	22,101
E-106	22,146
E-107	22,312
E-109	21,756
Hex I	25,756
Hex II	21,580
Hex III	24,934
Hex IV	21,585
Hex V	20,187
C1	41,529
C2	23,074
H1	22,312
Total	6,125,186

**Table 5.6:** The price of the different equipment in the design without a reverse water gas shift reactor. PFR-100 is the methanol reactor, K-xxx is the compressors, and E-xxx is the heaters and coolers from Aspen HYSYS V9 (Aspen Technology, Inc.).

Equipment	Price [USGC 2007]
Separator (after methanol reactor)	16,994
Distillation column	119,531
PFR-100	94,692
K-100	993,115
K-102	702,690
K-103	702,690
K-104	991,231
K-105	991,231
K-106	991,231
E-101	54,648
E-102	20,428
E-103	22,055
E-104	22,098
E-105	22,103
E-106	22,128
E-100	69,292
Total	5,716,630



# Chapter 6

## Discussion

In this chapter the method shown in Chapter 3, the literature study in Chapter 4 and the result from Chapter 5 are discussed.

### 6.1 Design

In this thesis two designs were investigated to look into the possibility of producing methanol from  $\text{CO}_2$  extracted from seawater. Both designs consists of a chain of compressors, a methanol PFR, a separator and a distillation column, the RWGS design has in addition to this, a reactor where the RWGS reaction takes place and a separator to extract water before the methanol PFR. By pre-processing the feed stream it is possible to extract water before entering the methanol reactor pushing Equation (2.3) to the right, resulting in an increase in the product yield. This could also be used to decrease the size of the methanol reactor and keep the same yield as using one reactor.

The conversion ratio of both designs is rather good. Seen in Table 5.2, the conversion ratio for the RWGS reactor is 98 % with the RWGS reactor, and 96 % without. Compared with the carbon conversion ratio from methanol production from syngas this is quite high, as the normal syngas conversion ratio is around 75-80 % [7]. The purity of the two designs are 99 % and 96 % for the design

with the RWGS reactor and without the RWGS reactor respectively. This shows that the conversion ratio with the RWGS reactor is not only larger than without the reactor, but also purer. Both the designs deliver crude methanol up to the desired standards, 94-99 % [7]. Table 5.2 also shows a lower product flow in the design with the RWGS reactor, however, the purity of the product is higher, so the total amount of methanol yielded is consequently larger in this stream.

## 6.2 HYSYS

Aspen HYSYS V9 (Aspen Technology, Inc.) calculates step by step instead of calculating the whole process at once, therefore there will always be errors in the calculations. As a consequence, the imbalance in the calculations should be considered. In the design with the RWGS reactor, there is a loss of 3.518 kg/h, which corresponds to a relative imbalance of 0.11 %. In the design without the RWGS reactor, the imbalance is 8.774 kg/h loss, which corresponds to a relative imbalance of 0.31 %. This shows that there might be some errors in the calculations that could affect the final results. However, the imbalance of both designs are quite small compared to the total production of over 1,700 kg/h, and is assumed insignificant.

When choosing an equation of state property package it is important to choose a package that fits well in the temperature and pressure range for the given case. It is also important that the property package is suited to work on the compounds used in the design. The Peng-Robinson package was used as this package has a high range of temperature and pressure. This package is good at calculating with hydrocarbons, which fit well with the cases we looking at making the Peng-Robinson package a suitable choice.

## 6.3 Optimization

Optimization is used to find the optimal conditions for the designs. The optimized  $H_2/CO_2$  ratio shown in Table 5.1 was found to be 3, which corresponds with the ratio given in Equation (2.3). However, this is at steady state, and there may be more advantageous to have a higher amount of  $H_2$  as this would make the reaction

go faster and possibly have a higher yield. One possibility is to insert  $H_2$  at several places in the reactor making the concentration higher as the reaction goes on. As for the temperature and pressure, these corresponds well with the temperature and pressure used in most methanol production today [20].

## 6.4 Heat Integration

To make the plant more energy efficient a heat integration system was proposed for the system with the RWGS reactor, shown in Figure 5.2. There are several designs that could have been considered, but as the plant are located on a floating unit, there is limited space making it important to develop the design of the heat integration network as small as possible. To minimize the space taken up by heat exchangers, streams with a large temperature difference were chosen because of the extensive driving force.

A heat integration network lowers the energy consumption, however, it increases the investment cost. The increased cost is often worth it, as energy will have a high cost resulting in high running cost. The heat integration network for the RWGS case, shown in Figure 5.2, increases the energy efficiency by reusing heat that would have been lost.

## 6.5 Cost

As seen in Table 5.4, the diameter of the separators is at the minimum making them equally large for both designs. The size of the distillation column is calculated from data obtained from Aspen HYSYS V9 (Aspen Technology, Inc.). This data is similar for both designs resulting in the same size of the columns as well.

Because the design with the RWGS reactor has an extra reactor, an extra separator, and three extra heat exchangers, the price for this design automatically increases. The question is then if the increase in price for the equipment can be accepted for the marginally better product. The RWGS reactor design produces 37.4 kg/h more methanol than the design without the RWGS reactor. If the price of methanol is assumed to be 400 USD per metric ton [25], and the methanol sold is the pure

methanol stream, the difference in profit would be 131,049 USD more per year. This would after just over three years have made up for the difference in equipment cost. However, there would also be an increase in operating cost from increased power usage that has to be considered.

Many chemical processes produces side-products, which can be sold as an extra source of income. As a result of the high CO<sub>2</sub> content, both the designs will have side-products, which could be sold, resulting in a higher income for the plant, these includes dimethyl ether, higher alcohols (ethanol, propanol), and higher alkanes (ethane, propane) [9]. There will also be a surplus of pure O<sub>2</sub> gas that can be sold that could be sold to further increase profit. To make use of these side products there might have to be made additional investments for extracting them. This is something that has to be taken into consideration when building the plant.

## 6.6 Methanol Production

Methanol production is usually produced from natural gas, where the natural gas is transformed using a steam reformer and an autothermal reformer. The synthesis gas is then transformed into methanol in a methanol reactor. The difference, between the method used in methanol production today and the methods used in this thesis, is the syngas production. The syngas in this thesis is made by converting CO<sub>2</sub> into syngas using the reverse water gas shift reaction. The rest of the production is the same as for traditional methanol production. The other design looked at has no RWGS reactor, so the methanol reactor converts methanol directly from CO<sub>2</sub>. Because of the energy from solar panels on floats around the floating unit, there is possible to make methanol from 100 % renewable sources for both designs.

The total yearly demand of methanol in 2015 was 75 million metric tones and it is increasing [26]. The yearly production of the two designs explored in this thesis is 15,476 tons for the design with the RWGS reactor and 15,148 tons for the design without the RWGS reactor. The two designs both produce about 0.02 % of the yearly demand of methanol. So to cover the entire demand of methanol about 5,000 plants of the same magnitude would be required. In comparison Equinor's methanol plant at Tjeldbergodden produces 900,000 tons methanol yearly [27], which make up 1.2 % of the yearly demand of methanol.

## 6.7 Literature Study

As mentioned, a study has previously looked into two similar models of methanol production as in this thesis. The reason why it is still interesting to investigate it further is because Anicic et al. [14] used captured CO<sub>2</sub> on a land based plant and buying electricity. In this thesis, the plant is located on the ocean, as there is a lot of space and access to all the resources needed. The CO<sub>2</sub> feed is extracted from seawater, and the electricity is produced using islands of floating solar panels. These changes might have impact on the sizing and cost of the plant.

The results of this thesis, shown in Table 5.2, shows that the design with the RWGS reactor produces slightly more methanol than the design without the RWGS reactor. This is different from the result found by Anicic et al. [14], which concluded that the direct design has a higher production of methanol resulting in a better economic efficiency. Even if the results are different, the difference in methanol production is small in both this thesis and in Anicic et al. [14]. In this thesis, both designs seem to perform at approximately the same level, which is the same conclusion that Anicic et al. arrived at [14].

Anicic et al. designed a much larger plant. The production of methanol is 25,270 kg/h in the design with the RWGS reactor, and 28,714 kg/h in the design without. This is a difference of over 3,000 kg/h which is quite a small difference compared to the total production. As the plant in this thesis produces CO<sub>2</sub> from seawater through a membrane, the feed stream is significantly smaller, resulting in a much smaller product stream as well. This will increase the cost of the equipment compared to the amount of methanol produced.

The fact that the design without the RWGS reactor produces more methanol in Anicic et al. [14], compared with this thesis where the pre-processed design with the RWGS reactor produces more methanol, can be explained by the fact that in Anicic et al., the design without the RWGS reactor still uses two reactors, with a flash tank to remove the methanol [14], where as the design without the RWGS reactor in this thesis only uses one reactor. This causes the conversion rate of CO<sub>2</sub> in Anicic et al. to be much higher. This could be the reason why the design without the RWGS reactor produces more methanol, resulting in better efficiency. The design without the RWGS reactor in this thesis could also add a second reactor

to increase the output of methanol, but that would also increase the investment cost. The decision to add two reactors is therefore a choice that have positive effects for the methanol production, but negative effects for the investment costs.

The designs in this thesis are planning to use solar panels for electricity, therefore the driving cost of the electricity is assumed to be zero. Anicic et al. assumes the costs of the reactants is connected to the price of electricity. As the designs of this thesis should be independent of the price of electricity, and only an investment in solar panels, this could be a huge save in production cost, and therefore be an advantage. The lower expense in production cost could make it profitable to sell the methanol at a lower price, and therefore more likely to be profitable.

## 6.8 CO<sub>2</sub> Reduction

The aspect of the amount of CO<sub>2</sub> emission is important in a climate perspective, but this could also have a direct effect of the cost of the plant, because of taxes related to emissions of greenhouse gasses. As for the CO<sub>2</sub> emission, the production has a 100 % reduction in emission using this plant compared to a traditional plant. However, this is a small-scale plant and the economical investments makes it quite expensive compared to traditional plants. According to the IPCC there should be a net zero emission of CO<sub>2</sub> in 15 years [2]. To make this goal of net zero emission of CO<sub>2</sub> there has to be implemented drastic changes. These changes could include extra taxes on CO<sub>2</sub> emission resulting in a higher price on chemicals like methanol. Taxes on CO<sub>2</sub> in Norway are, as of 01.01.2018, 500 NOK per metric ton [28], this is approximately 15 % of the price of methanol today. An increase of the tax could in turn make this method of producing methanol from CO<sub>2</sub> more profitable.

Szima et al. stated that the price of methanol should double to make it profitable to produce methanol from CO<sub>2</sub>. In this thesis both the designs evaluated are using electricity from solar panels, reducing the production cost of the designs. The fact that the production does not have to pay CO<sub>2</sub> tax, as the production extracts the CO<sub>2</sub> from the seawater, decreases the production cost further. From this it can be assumed that the production will be profitable with under a doubling of the methanol price. If the taxation on CO<sub>2</sub> increases further, the price of methanol increases, and will make it even closely that the production is profitable.

## 6.9 Future Work

The feasibility of the technology looks like it has potential, however, further research is needed in some areas.

The kinetics used in the methanol reactor are normally used in calculations with much less CO<sub>2</sub> in the feed gas. This should be considered as this may change the conversion ratio of carbon [29]. A kinetic model that considers the elevated levels of CO<sub>2</sub> should therefore be implemented.

There should also be made a complete cost estimation, with cost such as equipment for electrolysis of water, solar panels for energy, and operating cost. To get a complete overview of the cost, and how profitable it can be to convert CO<sub>2</sub> into methanol.

The feed streams capacity to deliver CO<sub>2</sub> is dependent on the Eisaman BPMED cell. Other possible extraction method of CO<sub>2</sub> should therefore also be considered, and the possibility of increasing the feed stream by installing several cells.





## Conclusion

In this thesis, the feasibility of a floating methanol production plant was investigated. The plant was simulated in Aspen HYSYS V9 with two different designs, one with a RWGS reactor, and one without. A heat integration network was developed for the design with the RWGS reactor. It was found that the design with the RWGS reactor had a purity of 99 % and a carbon conversion ratio of 98 %. The design without the RWGS reactor had a purity of 96 % and a carbon conversion ratio of 96 %. The difference in cost of equipment was found to be approximately 410,000 USD. However, the RWGS design produces 327,624 kg more methanol per year, resulting in a difference in profit of 131,049 USD.

As for the feasibility of the technology, it looks like it has a great potential because of the high conversion ratio of carbon, and the purity of the raw product.

The price of the plant is quite high, but with production of electricity from solar panels, the operating cost can be cut down fairly.



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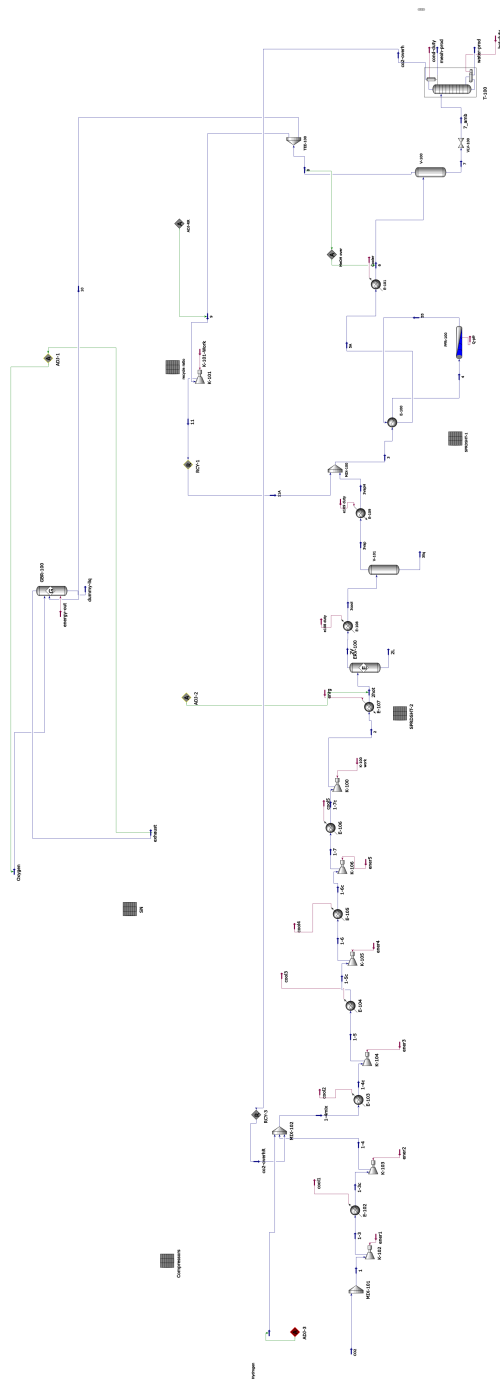
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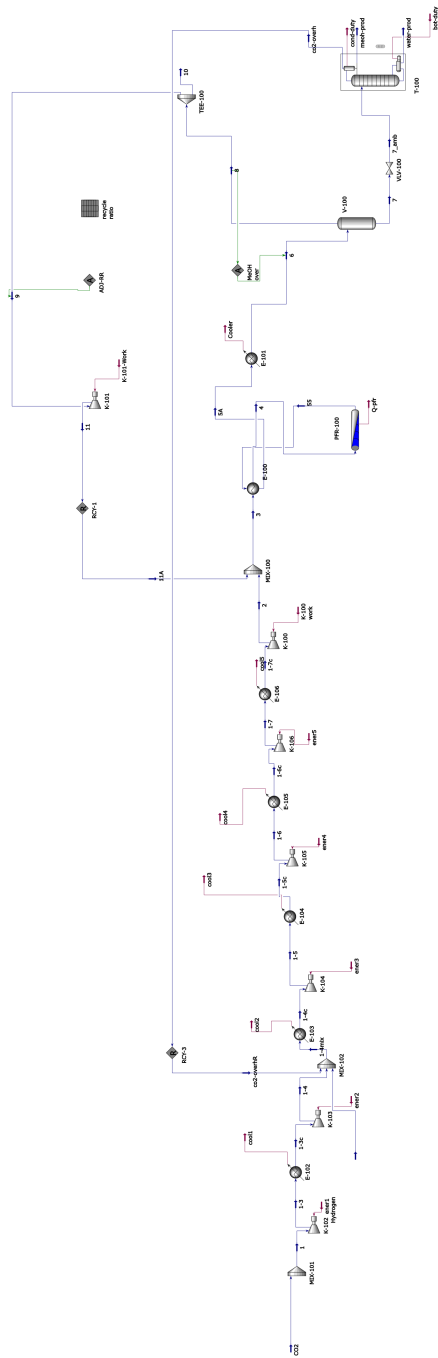
# Appendix

## A HYSYS Flowsheet



**Figure 1:** Flowsheet of the design with reverse water gas shift reactor.





**Figure 2:** Flowsheet of the design without reverse water gas shift reactor.

