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Techno-economic feasibility study of a methanol plant using carbon dioxide and hydrogen

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Abstract

In 2015, more than 80% of energy consumption was based on fossil resources. Growing population especially in developing countries fuel the trend in global energy consumption. This constant increase however leads to climate change caused by anthropogenic greenhouse gas (GHG) emissions. GHG, especially CO₂ mitigation is one of the top priority challenges in the EU. Amongst the solutions to mitigate future emissions, carbon capture and utilization (CCU) is gaining interest. CO₂ is a valuable, abundant and renewable carbon source that can be converted into fuels and chemicals. Methanol (MeOH) is one of the chemicals that can be produced from CO₂. It is considered a basic compound in chemical industry as it can be utilised in a versatility of processes. These arguments make methanol and its production from CO₂ a current, intriguing topic in climate change mitigation.

In this master's thesis first the applications, production, global demand and market price of methanol were investigated. In the second part of the thesis, a methanol plant producing chemical grade methanol was simulated in Aspen Plus. The studied plants have three different annual capacities: 10 kt/a, 50 kt/a and 250 kt/a. They were compared with the option of buying the CO₂ or capturing it directly from flue gases through a carbon capture (CC) unit attached to the methanol plant. The kinetic model considering both CO and CO₂ as sources of carbon for methanol formation was described thoroughly, and the main considerations and parameters were introduced for the simulation. The simulation successfully achieved chemical grade methanol production, with a high overall CO₂ conversion rate and close to stoichiometric raw material utilization. Heat exchanger network was optimized in Aspen Energy Analyzer which achieved a total of 75% heat duty saving.

The estimated levelised cost of methanol (LCOMeOH) ranges between 1130 and 630 €/t which is significantly higher than the current listed market price for fossil methanol at 419 €/t. This high LCOMeOH is mostly due to the high production cost of hydrogen, which corresponds to 72% of LCOMeOH. It was revealed that selling the oxygen by-product from water electrolysis had the most significant effect, reducing the LCOMeOH to 475 €/t. Cost of electricity also has a significant influence on the LCOMeOH, and for a 10 €/MWh change the LCOMeOH changed by 110 €/t. Finally, the estimated LCOMeOH was least sensitive for the change in cost of CO₂. When comparing owning a CC plant with purchasing CO₂, it was revealed that purchasing option is only beneficial for smaller plants.

Keywords methanol, CCU, CO₂ hydrogenation, simulation, Aspen, economics, levelised cost

Foreword

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Nomenclature

Abbreviations

CAMERE	Carbon dioxide hydrogenation to form methanol via a reverse-watergas-shift reaction
CAPEX	Capital expense
CC	Carbon capture
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CEPCI	Chemical Engineering Plant Cost Index
CRI	Carbon Recycling International
CTO	Coal-to-olefins
DCC	Direct contact cooler
DME	Dimethyl ether
DMFC	Direct methanol fuel cell
EBITDA	Earnings before interest, taxes, depreciation and amortization
FCI	Fixed-cost investment
GHG	Greenhouse gas
HC	Hydrocarbon
ICE	Internal combustion engine
IMFC	Indirect methanol fuel cell
IRENA	International Renewable Agency
LCOH ₂	Levelised cost of hydrogen
LCOMeOH	Levelised cost of methanol
LHHW	Langmuir-Hinshelwood-Hougen-Watson
LPG	Liquefied petroleum gas
LPMeOH	Liquid-phase methanol
MEA	Monoethanolamine

MeOH	Methanol
MTBE	Methyl tert-butyl ether
MTG	Methanol-to-gasoline
MTO	Methanol-to-olefins
MTP	Methanol-to-propylene
NPV	Net present value
NRTL	Non-random two-liquid model
OPEX	Operating expenses
PEC	Purchased equipment cost
PEM	Polymer electrolyte membrane
PM	Particulate matter
RK-SOAVE	Redlich-Kwong-Soave equation of state
RWGS	Reverse water-gas shift
SOFC	Solid oxide fuel cell
STY	Space time yield
TAME	Tertiary amyl methyl ether
TCI	total capital investment

Symbols

C	cost of equipment
E_a	activation energy
f	concentration exponent
GHSV	gas hourly space velocity
I	cost index
K	constant
k	pre-exponential factor
kg/(L _{cat} h)	kilogram of methanol produced per litre of catalyst hourly, unit of STY

n	temperature exponent
ppm	part per million
R	gas law constant
r	rate of reaction
t/a	ton per annum
t/d	ton per day
t/h	ton per hour
T	absolute temperature
T ₀	reference temperature
X	primary design variable characterizing the size of the equipment
wt%	weight percentage
α	scaling exponent

1 Introduction

Ever since the industrial revolution human development has been greatly linked to the ever-increasing consumption of fossil energy resources. These energy resources have paved the way to our current technological development. These resources not only provide heat, electricity, and transportation, but are also converted to pharmaceuticals, hygiene products, plastics, fertilizers. Life without these products and services would be impossible and unthinkable for many humans. [1]

Since 1991, the total global energy consumption has increased by more than 50%. In 2015, more than 80% of energy consumption was based on fossil resources. [2] Growing population especially in developing countries which is coupled with growing consumption for products and services fuel the trend in global energy consumption. This constant increase however has adverse effects on the environment and therefore our lives. Climate change due to anthropogenic greenhouse gas (GHG) emissions and its mitigation has been on the agenda of world leaders since the Kyoto Protocol. [1]

The European Union has pledged to reduce its GHG emissions by 80% below its 1990 level by 2050. This grandiose target is planned to be reached by a series of policies and directives extending to all industries and sectors. Some of the most important methods to achieve these targets are increasing the share of renewables in the energy sector, and utilization of biofuels not only in road transport, but also in aviation. The introduction of obligatory carbon capture and storage (CCS) applications in industries where CO₂ emissions are inevitable. This could lead to a European Union by 2050 that is less dependent on gas and oil imports, and is a leading power in clean technologies. [3]

Amongst the solutions to mitigate future emissions, carbon capture and utilization (CCU) is gaining interest, as compared to CCS it is less controversial [4]. CO₂ is a valuable, abundant and renewable carbon source that can be converted into fuels and chemicals. Currently the industrial use of CO₂ is very limited corresponding to only 0.6% of global CO₂ emissions [5]. CO₂ is a highly stable compound having low reactivity. Activating CO₂ is therefore an energy intensive process and its chemical utilization constitutes an important challenge. [6] CO₂ conversion via hydrogenation coupled with renewable energy could fulfil the increasing demand for transportation fuels and carbon-containing products [7]. The overall goal of these processes would be to reduce anthropogenic CO₂ emissions and overcome fossil fuel shortages by capturing CO₂ from the atmosphere through recycling it using renewable energy [8].

Methanol (MeOH, CH₃OH) is one of the chemicals that can be produced from CO₂. It is considered a basic compound in chemical industry as it can be utilised in a versatility of processes. Due its high energy content it acts as energy carrier, while its compatibility with liquid transportation fuels makes it suitable for fuel blending. Recent developments in the petrochemical industry have made methanol a relevant feedstock for the production of ethylene and propylene, the base materials for plastic products. Therefore, the expected global demand for methanol is constantly increasing. These arguments make methanol and its production from CO₂ a current, intriguing topic in climate change mitigation. [9]

1.1 Methodology and objective

The thesis consists of two main parts. First, a literature and technology review is conducted about methanol, its applications, especially focusing on the chemical and petrochemical industry, and its potential demand in the future. Then the conventional synthesis of methanol is investigated, and compared to a novel synthesis process where carbon dioxide is catalytically hydrogenated.

In the second part of the thesis, a methanol plant is simulated using Aspen Plus, where chemical grade methanol is synthesised from exhaust carbon dioxide and hydrogen produced by water electrolysis. First, a short literature review is collected of recent similar cases and simulations. It is followed by the detailed description of the process simulation of the methanol plant. Methanol plant with three different capacity is simulated in order to study the potential effects of scaling. In addition, the option of buying carbon dioxide or owning a carbon capture (CC) plant attached to the methanol plant are investigated.

In the economic part of the simulation, capital expenses (CAPEX) and operating expenses (OPEX) are presented in order to compare the production cost for each size and option. Finally, the estimated levelised cost of methanol (LCOMeOH) is compared to the current fossil methanol price. A subsequent sensitivity analysis examines the impact of oxygen selling option, different electricity prices and carbon dioxide sources on LCOMeOH.

The objective of the thesis is to investigate the techno-economic feasibility of a methanol synthesis plant where carbon dioxide and hydrogen are used as feedstock. The five main questions the thesis intends to answer are:

1. What is the potential demand for methanol in the chemical and petrochemical industries?
2. What are the current, commercially available technologies used for carbon dioxide hydrogenation to produce methanol?
3. How does the setup of a CO₂-based MeOH plant look like?
4. What is the LCOMeOH produced via CO₂ hydrogenation?
5. How do the most important cost parameters influence the LCOMeOH?

2 Methanol

Methanol (CH_3OH) is a versatile chemical compound that can serve as a hydrogen and energy carrier, fuel, and as raw material for the chemical and petrochemical industries [9]. Methanol is a colourless, water-soluble liquid that has mild alcoholic odour, therefore its other names are methyl or wood alcohol [1].

Methanol has a heating value between 19.66 and 22.2 MJ/kg that makes it a valuable energy source. Compared to methanol gasoline and diesel have twice the energy content at around 44 MJ/kg, while hydrogen stands at 143 MJ/kg. Boiling and melting point of methanol are at 65 °C and -96 °C respectively, which makes it easy to store, transport and distribute in liquid form in tank cars or pipelines. [1]

Methanol is highly toxic for humans if inhaled or absorbed orally, and can lead to blindness and in worst case even to death. Therefore, methanol has to be handled and stored with care, especially as it can be mixed up with ethanol due to their similar characteristic. Compared to regular fuels it is less toxic, and it is not carcinogenic. At the same time methanol is not environmentally toxic, it is biodegradable and does not accumulate in the environment as opposed to diesel and other regular fuels. [9]

This chapter describes the applications of methanol focusing on the chemical and petrochemical industries, its current and forecasted demand. It is followed by a comparison of current market price of fossil methanol with production cost from various feedstock. The chapter ends with a detailed summary of conventional methanol production and its comparison with CO_2 -based methanol production.

2.1 Applications of methanol

Methanol is used in a wide variety of products and it is considered a base chemical compound in the chemical industry (Figure 2.1). Due to its high energy content at 22.2 MJ/kg, it can serve as energy carrier as well as hydrogen carrier. It is used as transportation and industrial fuel for internal combustion engines (ICEs) and household appliances, it can replace gasoline, diesel and natural gas. It can be used in fuel cells as well. In addition, it stores energy more conveniently and safely than hydrogen or methane due to its liquid state. [1]

The produced methanol can have different purity levels depending on the requirements determined by the type of application (Table 2.1). Crude or raw methanol can be used in some processes, which means that the methanol is used without distillation. After distillation the following three purities exist: fuel grade, “A” grade, and “AA” grade (purity exceeding 99.85%). [10]

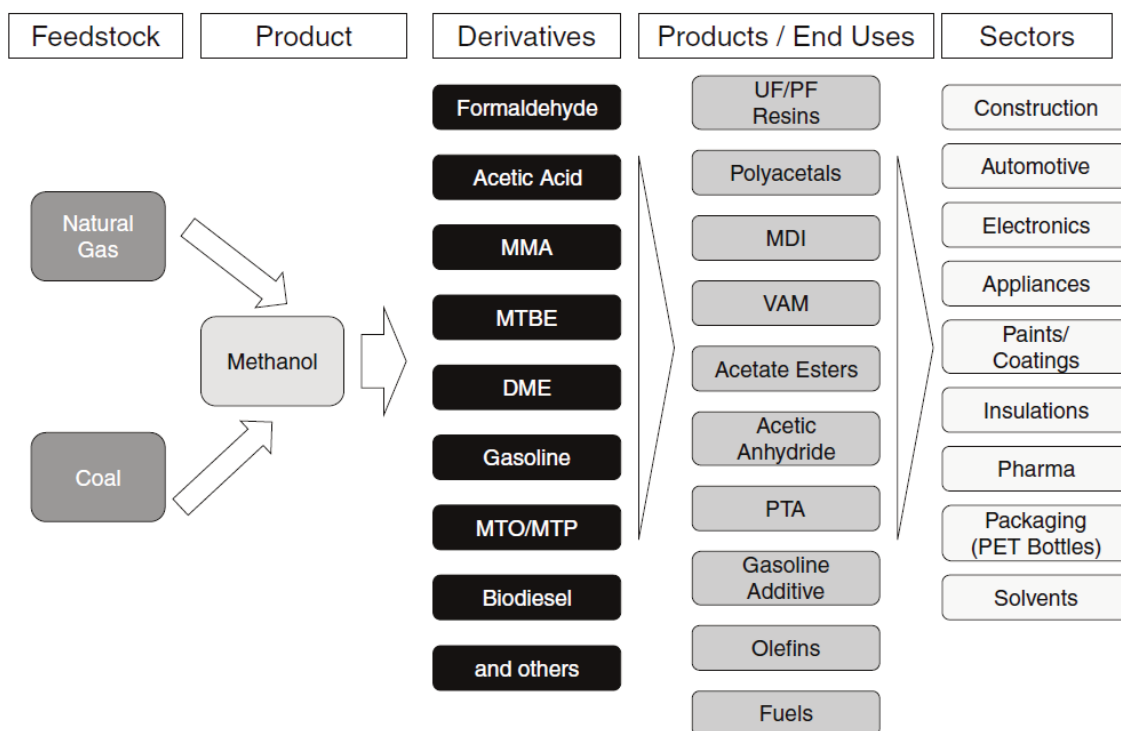


Figure 2.1: Value chain of methanol [9]

Important industrial reactions of methanol include the following [11]:

- Dehydrogenation and oxidative dehydrogenation
- Carbonylation
- Esterification with organic or inorganic acids and acid derivatives
- Etherification
- Addition to unsaturated bonds
- Replacement of hydroxyl groups

Table 2.1: Purity requirement of methanol for different applications

<i>Application</i>	<i>Purity requirement of methanol</i>	<i>Purity [wt%]</i>	<i>Comments</i>	<i>Reference</i>
MTO/MTP/MTG	Crude methanol	N/A	Process through DME	[9]
DME	Crude methanol	N/A	Can be produced from syngas directly as well	[12]
Chemicals including formaldehyde and acetic acid	“AA” grade	99.85		[1, 10]
Solvent	“A” grade	N/A		[10]
Fuel (pure or blend)	Fuel grade	99.7		[1]

2.1.1 Methanol in the chemical industry

Methanol is one of the most important materials utilized by the chemical industry [9]. There is a wide variety of end-products that use methanol at some point of their production process. These products include paints, solvents, engineered wood, plastics, PET bottles, safety glass, carpets, mattress foam, fertilizer, and furniture using resins. [12, 13]

The two most important chemicals based on methanol are formaldehyde and acetic acid, as these consume together almost 40% of the total methanol supply [13].

2.1.1.1 Formaldehyde

Production of formaldehyde consumes almost one third of the current methanol supply [13]. It is also an important compound in the chemical industry as several other industries use it in their production processes. These industries include construction, textiles, carpeting and wood processing industries.

Methanol can be converted to formaldehyde in three different processes using one of the two catalytic technologies. The first process is oxidative dehydrogenation where methanol and oxygen pass over a thin bed of silver catalyst at 600-720 °C. This process can be done both single-pass at the lower end of the indicated temperature range, or with recycle at the higher end of the temperature range. [9]

In the second process called methanol oxidation, methanol and oxygen are reacted over a molybdenum and iron oxide catalyst at 250-400 °C. Even though this process requires lower temperature, still the oxidative dehydrogenation is the more widely used one. [9]

2.1.1.2 Acetic acid

Acetic acid is the second most important chemical that needs methanol for its production. Currently almost all acetic acid is made through methanol carbonylation. This process replaced the less economic acetaldehyde oxidation production process. [9]

Acetic acid is mostly converted to vinyl acetate that is used in the production of a wide range of polymer-based products such as paints, adhesives and foam rubber. Acetic acid can be also converted to terephthalic acid, which is the basic compound for the production of PET bottles and nylon fibres. [12]

2.1.2 Methanol in the petrochemical industry

Methanol conversion to hydrocarbons was first invented in 1970s, and since then gained considerable interest especially in China in the last decade. Out of the three processes, MTG, MTO and MTP, the second is regarded as the most widespread. Methanol demand for MTO increased from 0% of global methanol consumption in 2009 to 15% by 2017. [9, 13]

In this sub-chapter, a short summary of the three processes is presented in chronological order of their invention. Table 2.2 summarizes and compares the three processes.

Table 2.2: Summary of MTG, MTO and MTP processes, * depends on type of reactor and operating conditions [9]

	<i>MTG</i>	<i>MTO</i>	<i>MTP</i>
<i>Catalyst</i>	ZSM-5	SAPO-34 ZSM-5	ZSM-5
<i>Temperature</i>	300-450 °C	350-525 °C	480 °C
<i>Pressure</i>	1 bar	2.2-3.5 bar	1.3 bar
<i>Main product</i>	Gasoline (~87 wt%)*	Propylene (~33 wt%)* Ethylene (~26 wt%)*	Propylene (~66.5 wt%)* Gasoline (~25 wt%)*
<i>Main by-products</i>	LPG (~13.6 wt%)* Fuel gas (~1.4 wt%)*	Gasoline (~29 wt%)* Fuel gas (~2 wt%)*	LPG (~5 wt%)* Ethylene (~2.8 wt%)*

2.1.2.1 Methanol-to-gasoline process

High-quality gasoline can be produced from methanol by a process called methanol-to-gasoline (MTG) discovered in the 1970s by Mobil (now ExxonMobil) [9]. It is regarded as one of the most important processes for alternative liquid fuel production along with the Fischer-Tropsch process from the 1920s. The produced gasoline fulfils all the requirements for conventional gasoline with regards to octane number, emissions, cold start behaviour and driveability. The currently only known catalyst for MTG process is the one developed by Mobil called ZSM-5. The process takes place at temperatures between 300-450°C and pressure at 1 bar. Both fixed-bed and fluidized-bed reactor designs exist; however, only plants using fixed-bed reactors are on commercial scale. It is reported that the MTG process using fluid-bed has lower investment cost, and is more economical due to heat recovery compared to the fixed-bed MTG process [14]. The product gasoline has low sulphur and benzene content, and fulfils EU and US gasoline standards. [9]

ExxonMobil's fixed bed MTG multi-reactor system (Figure 2.2) first partially converts the methanol feed to DME, then the DME/methanol mix is fed into the MTG reactor. The products, raw hydrocarbons and water are separated, followed by a de-ethanizer to remove LPG fractions from gasoline. Then, the gasoline is separated into light and heavy fractions, while the heavy fraction is further treated to reduce durene content to 2 wt% [15]. The process yields 56 wt% water and 44 wt% hydrocarbons, out of which 87 wt% is gasoline, the rest is mostly LPG. ExxonMobil constructed the first commercial MTG plant (600 kt/a) coupled with gas reforming and methanol synthesis plant in New Zealand which operated between 1985 and 1997. They opened another MTG plant (100 kt/a) in China using coal for methanol production in 2009. By 2014, ExxonMobil has licensed six MTG plants across China and USA producing close to 6 million t/a gasoline, and currently piloting fluid bed MTG processes. [14]

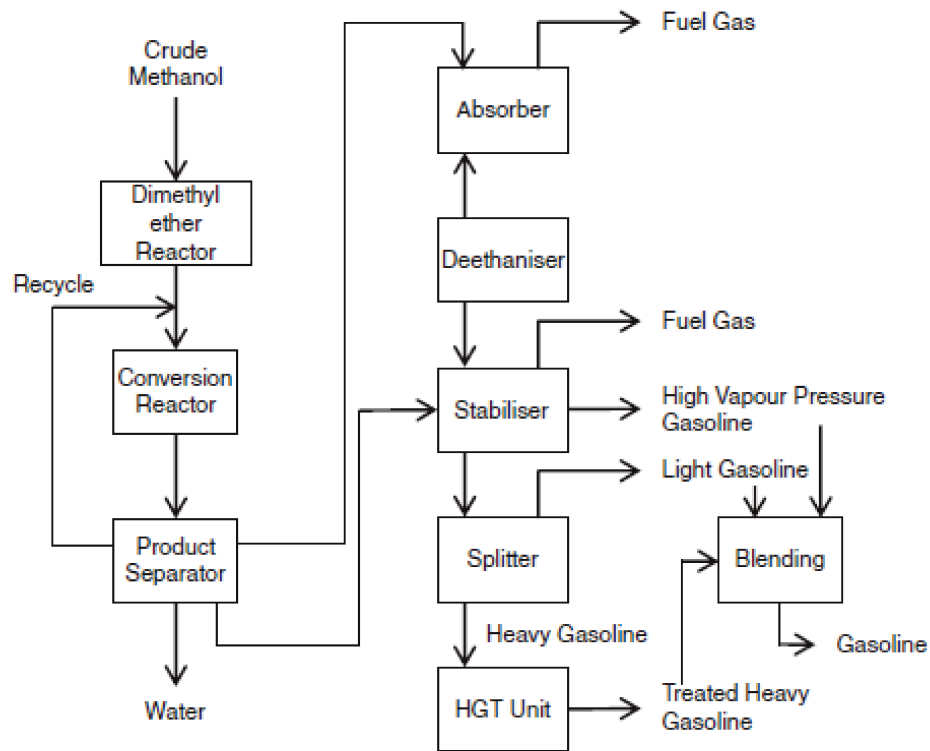


Figure 2.2: Schematic flow diagram of the fixed-bed methanol-to-gasoline process [9]

Haldor Topsøe [16] offers MTG technology using methanol or DME as feedstock to produce high-octane gasoline fraction suitable as direct drop-in fuel that satisfies requirements established by the Euro V vehicle emission standard.

2.1.2.2 Methanol-to-olefins

The methanol-to-olefins (MTO) process is based on improved selectivity of the MTG process towards olefins on ZSM-5 zeolite. Light olefins, such as ethylene and propylene are used to produce the most important commodity plastics like polyethylene and polypropylene (Figure 2.3) [9]. Currently olefins are mainly produced from fossil fuels, primarily natural gas or crude oil, by steam cracking which is a well-established process both economically and technologically. With the recent discovery of abundant shale gas, where ethane is a by-product from methane production, ethane steam crackers are becoming the new norm for ethylene production shifting from naphtha crackers. However, steam cracking is highly selective towards ethylene, and propylene has to be sourced from other feedstock. [17]

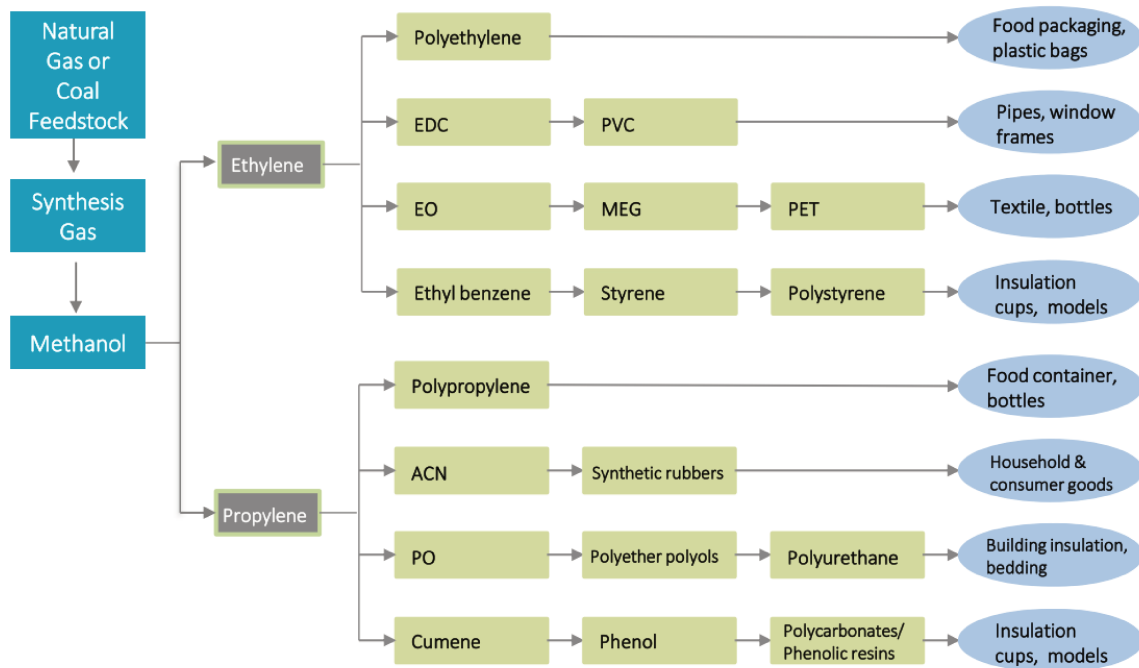


Figure 2.3: Chemicals and end-products produced by MTO process [13]

Other routes for light olefin production are fluid catalytic cracking and dehydrogenation of paraffin. The MTO process compared to them offers lower energy consumption and CO₂ emissions while producing polymer grade olefins. MTO applications present the possibility to replace crude oil with a variety of feedstock from natural gas and coal to biomass and CO₂. In order to successfully realize the MTO process, it has to become more efficient with less by-product generation (paraffin's and olefins with four or more carbon atoms). [9]

The first commercial scale MTO plant was constructed by Mobil in collaboration with Uhde in Wesseling, Germany in 1985. Currently, UOP/Hydro and ExxonMobil both use fluidized-bed reactor in their MTO process technology, however, the type of catalyst used is different. Union Carbide developed the SAPO-34 catalyst that is more selective than ZSM-5, but requires frequent regeneration due to coking. [9]

Research to investigate factors influencing lower deactivation in SAPO-34, such as operating temperature and crystal size is on-going [18]. SAPO-34 has reportedly 75-80% carbon selectivity, and by varying process conditions the propylene-to-ethylene ratio can be changed between 0.7 and 2 which is favourable in a fluctuating olefin market [17]. SAPO-34 produces both propylene and ethylene, while ZSM-5 mostly produces propylene [19]. MTO technology developed by UOP uses SAPO-34 catalyst [19] and offers a wide range of propylene-to-ethylene ratio between 1.3-1.8 [20]. UOP has further developed the process in collaboration with Total Petrochemicals, and introduced the integrated olefin cracking process, which transforms the C₄-C₆₊ by-products to lighter olefins. With this integrated process further 20% increase can be achieved in light olefin output, while the propylene-to-ethylene ratio reaches over 2.0 [21].

2.1.2.3 Methanol-to-propylene

As the demand for propylene is growing at a faster rate than ethylene, especially in China, processes specifically designed to produce propylene are necessary. The MTP process is

very similar to the MTO process, the major difference is the type of catalyst used and operating conditions [9]. The catalyst used in the MTP process is developed by Süd Chemie (now Clariant). It has 99% conversion rate of methanol/DME with maximum propylene selectivity, low coking tendency and very low propane yield. The catalyst needs to be regenerated after 500-600 operating hours. [22]

According to information from Lurgi [23], the developer of the MTP process, the process takes place at 1.3 bar pressure and at 480°C in a fixed-bed reactor. Fixed-bed reactor was preferred due to its lower investment cost and less-complicated scale up compared to fluid-bed reactors. The process yields 1410 t/d propylene, 540 t/d gasoline and 109 t/d LPG from 5000 t/d methanol. By-products of the process are 2800 t/d water, 60 t/d ethylene from the purge gas, naphthenes, paraffin and aromatic components.[22] However, Huang et al. [24] claims that the expected 65% propylene selectivity is not met in the Chinese plants, and the overall olefin selectivity is below 80%. According to their research, the low selectivity rate could be increased by lowering the residence time in the reactor, and decreasing the diameter of the catalyst pellet.

Propylene purity of 97% is necessary to qualify as a polymer grade feedstock. Borealis successfully polymerized and tested the propylene from Lurgi's MTP, which used methanol from natural gas [22, 25].

2.1.2.4 Current availability of MTG, MTO and MTP plants

MTO and MTP projects are mostly realized in China combined with coal-to-methanol processes due to abundant cheap coal and growing demand for propylene. The production cost of propylene from coal in China is comparable to natural gas based projects in the Middle East. However, production of ethylene is still much cheaper in gas crackers in the Middle East [9]. The annual capacity of UOP's MTO technology reached 3.5 million metric tons in China by 2016 from 9 plants [26].

According to Chen et al. [21], from 2005, Europe could be a good location for MTO plants, as European petrochemical industry uses mostly naphtha for light olefins, which is dependent on crude oil prices. Ideally, methanol would be produced outside of Europe, where natural gas is cheap, and then shipped to MTO plants. With the current mega-scale methanol plants, that produce 5000 t/d, methanol could be available to European markets below 68 €/t. This is below the 78 €/t price that could make MTO plants more attractive than crude oil based olefin production, depending on the current crude oil market price. Another challenge in the European market that MTO plants would address is the propylene gap.

Xiang et al. [27] calculated that 78% of the MTO product cost is the raw material. They also argued that coal-to-olefin (CTO) plants, which have integrated MTO plants, are a good solution if co-fed with natural gas or coke oven gas, as CTO plants themselves have low investment costs. Moreover, the low energy efficiency and the high CO₂ emission can be improved by co-feeding.

Hannula et al. [28] calculated that the total capital investment of a UOP MTO plant producing 78.5 kt/a light olefins costs 37 million €. If coupled with an olefin cracker plant for 4 million € it would produce 15.5 kt/a light olefins additionally. The price of an MTO plant is twice of naphtha steam crackers producing the same amount of olefins due to the high cost of equipment. The maximum price for buying methanol for such MTO plants was

estimated to be 405 and 434 €/t, while in the methanol price on the European market was 408 €/t (currently, September 2018, it is 419 €/t [29]).

Lurgi has until 2015 licensed four 470 000 t/a MTP plants, out of which three is located in China, while the fourth licensed by BASF would be located in the US Gulf Coast [23]. The BASF project is currently on hold due to low prices for crude oil [30].

2.1.3 Other applications

Methanol is not only used in the chemical and petrochemical industries. Below a collection of other current applications can be found.

Methanol is an ideal transportation fuel for both internal combustion engines (ICE). Methanol and ethanol have been used as transportation fuels since cars were invented. One of the advantages of using methanol instead of gasoline is that it has higher octane number than gasoline, which means that it has higher compression ratio. Therefore, even though having half the energy content as gasoline, less than double the amount is enough to produce the same power output. [12]

Methanol can be used either as blend in regular fuels, or in pure form. The most important advantage of using blended gasoline or pure methanol in ICE or diesel engines is the reduction in CO₂ [8], and other emissions such as PM, NO_x, and HCs [12]. The drawback of using methanol blends is that vehicles have to be modified if the blend contains more than 15 vol% methanol due to corrosion. The currently used distribution infrastructure for gasoline can be used for methanol as well with slight modifications. [12]

Using methanol blends is common in China where not only M15 (15% methanol, 85% gasoline) are in effect but also M85 and M100 [10]. Methanol can be also converted to MTBE and TAME. MTBE is most widely used as blend for gasoline due to its high octane number. It can also be used as solvent, and be converted to high-purity polymer-grade isobutene. TAME is also a widely used octane booster [9]. Methanol also plays a significant role in biodiesel production as biodiesel is produced by transesterification of fats and oils with the help of methanol [9].

DME is made by methanol dehydration and has similar properties to LPG. DME can be mixed with a variety of fuels such as diesel and propane, and it provides low exhaust emissions of NO_x, with no sulphur and particulate emissions. DME is also an intermediate chemical in several processes including MTO/MTP/MTG and acetic acid. [9]

Methanol can also be used as fuel in fuel cells. There are two types of fuel cells running on methanol: direct methanol fuel cells (DMFCs), and fuel cells connected to methanol reformer, i.e. indirect methanol fuel cells (IMFCs). In the later, methanol is reformed over a Cu/Zn catalyst to reformat gas that contains hydrogen. This hydrogen is fed to the final fuel cell. A variety of fuel cells can be run directly on methanol such as alkaline fuel cells, PEM fuel cells and phosphoric acid fuel cells. Each type has its advantages and disadvantages, but this is not detailed further in this thesis. The main advantage of using fuel cells is that they have essentially zero emissions [8]. Compared to hydrogen-fuelled fuel cells the methanol-fuelled ones have the advantage of the fuel being in liquid form, therefore the storage of fuel is easier. [9]

DMFCs are applied in small, portable electronic devices like remote sensors, battery charging systems, scooters, forklift trucks [9]. Meanwhile IMFCs can be used in larger applications such as cars and ferries. A few example of this is Wärtsilä’s IMFC system using SOFC first time in the world to supply power for a car carrier vessel [31]. SerEnergy in Denmark also provides IMFCs for cars and vessels [32]. Moreover, a methanol filling station was opened recently in Aalborg, Denmark providing renewable methanol fuel produced by CRI for cars equipped with IMFCs [33].

Methanol can also be used in gas turbines after minor modifications. Such turbines are applied in the marine industry, as methanol has low emission rates; it is biodegradable and available worldwide. There are a number of vessels already equipped with engines supplied by Wärtsilä and MAN Diesel. [34]

2.2 Global methanol market and its cost of production

Methanol is a globally traded chemical that reached 75 million tons production last year. The global production is expected to reach 90 million tons by 2020 which is explained by the growing expansion of MTO technology especially in China [13]. Currently 15% of produced methanol is used by MTO processes, formaldehyde uses almost one third, while MTBE/TAME applications consume 12% (Figure 2.4 a).

Figure 2.4 b shows that beside Northeast Asia, meaning China, and other regions have close to constant demand for methanol. The rapid growth in China can be explained by the vehicle fleet running on methanol and the increasing demand for plastics. [13]

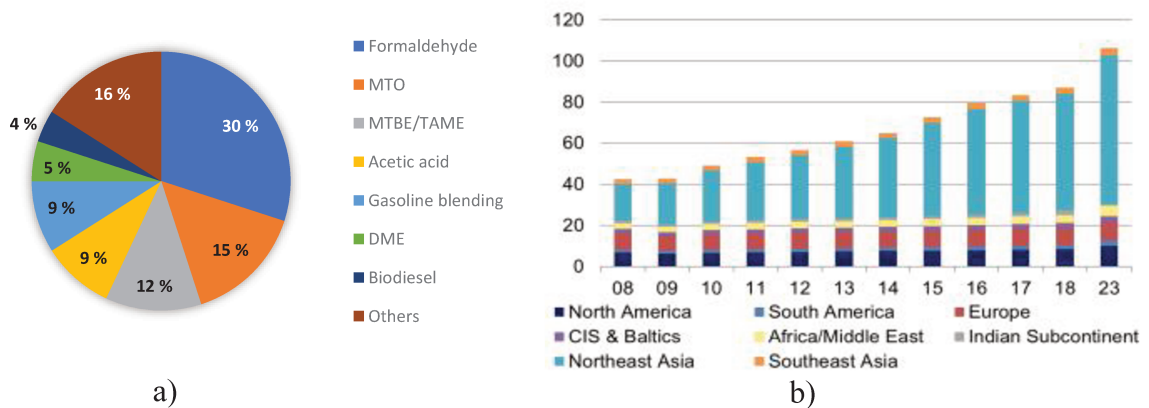


Figure 2.4: a) Global methanol demand by application in 2017 (on the right) [13], b) methanol demand by region in million tons (on the left) [35]

Figure 2.5 shows the quarterly posted price of methanol by Methanex, who is the world’s largest producer of methanol. Methanol produced by Methanex is based on natural gas. The current methanol price is the third highest in the last decade. There is a range of variables that influence the price of methanol, but it is mostly dependent on natural gas prices and availability, and also production availability of methanol plants. The current market price for conventional methanol stands at 419 €/ton (Sept 2018). [13, 29]

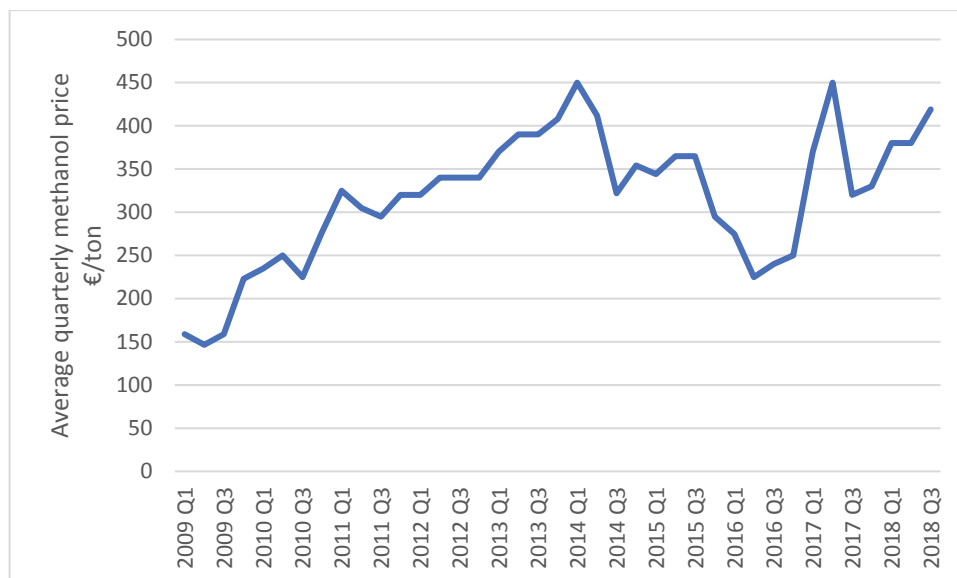


Figure 2.5: Methanex quarterly average European posted contract methanol price [29]

According to analysis by Boulamanti et al. [36] the average production cost of natural gas based methanol in 2013 in the EU was 408 €/t, while the price on the European market varied between 370-450 €/t. All the other investigated countries had lower production costs in the following order, from lowest to highest: Saudi Arabia, Russia, USA, and Ukraine. Russia, being a major exporter of methanol to the EU countries enjoys high margins compared to its 105 €/t production cost. The analysis discovered that the major contributor to the high production cost in the EU is the high cost of feedstock, which is almost four times higher compared to Russia's natural gas.

Production cost of petrochemicals in the EU ranges between 748 €/t and 816 €/t depending on whether the final product is only ethylene, or both ethylene and propylene, which is higher than the ones in USA or Saudi Arabia. However, transportation costs were not included in the analysis, which would make ethylene export from these countries less profitable. The global prices for ethylene and propylene in 2013 were 973 €/t and 1030 €/t respectively. [36]

A research done by IRENA [37] (Figure 2.6) shows the influence of feedstock and size of production plant on the production cost. It is clear that natural gas is the cheapest feedstock available for methanol production. Coal and wood can be considered second cheapest feedstock. However, they largely depend on the location of the methanol plant, and whether the raw material is available at low prices. It is also clearly visible that higher yearly output leads to lower production costs. However, plants with yearly outputs over 400 kt operate based on more traditional feedstock (natural gas, coal and wood). There are only a few existing plants using CO₂ as feedstock. Figure 2.6 also shows that such plants, the interest of this thesis, have one of the highest production costs, between 500 and 900 €/t. It can be observed that such plants positively benefit from scaling effect.

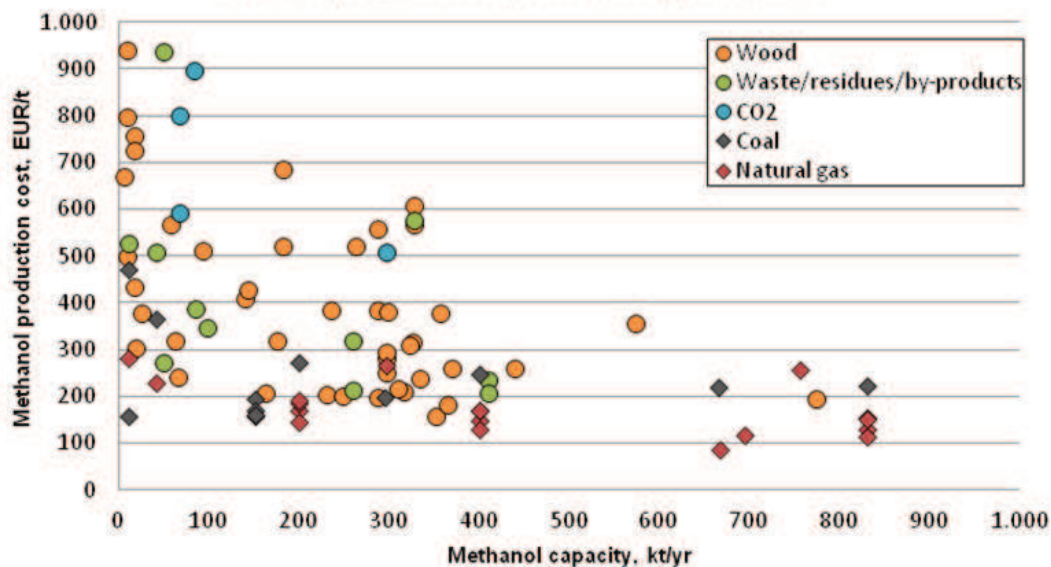


Figure 2.6: Production costs and production capacity of (bio)methanol for various feedstock [37]

2.3 Production of methanol

Methanol was discovered in the 17th century by Robert Boyle via wood distillation, which process continued to be the standard technology until the beginning of the 20th century when Sabatier introduced a synthetic method via reacting CO and H₂. The process, patented by BASF, was based on synthetic gas, which is a mixture of CO, CO₂ and H₂, produced via coal gasification. The reaction took place over a ZnO/Cr₂O₃ catalyst at high temperature and pressure (300-400°C and 250-350 bar). This process was highly inefficient and the following years concentrated on developing the process conditions, the catalyst, and cleaner syngas production. These developments had led to improved reaction conditions, first by reducing operating temperature and pressure to 300°C and 100 bar by ICI, followed by improvements by Lurgi lowering process temperature and pressure levels to 230-250°C and 40-50 bar. Currently syngas can be produced from a variety of carbon-based materials, from coal to biomass, the most common way globally being natural gas. [10]

Besides the conventional, syngas based methanol synthesis other state-of-the-art processes are emerging, however, these processes have not yet reached economic feasibility for scale-up due to low yields, selectivity, reaction conditions or environmental concerns. These technologies are [9]:

- Selective oxidation of methane via halogenation or via methyl bisulphate,
- High-temperature pyrolysis of methane followed by CO₂ hydrogenation,
- Enzymatic production from methane by methane-monooxygenase,
- Synthesis gas generated by hydrolysis of biomass feedstock,
- Co-electrolysis of CO₂ and water into syngas,
- Steam reforming or direct hydrogenation of glycerol.

In this sub-chapter, the conventional catalytic synthesis of methanol from syngas will be described, followed by a techno-economic description of and comparison to methanol production from CO₂ hydrogenation via water electrolysis.

2.3.1 Conventional synthesis of methanol

The conventional production of methanol consists of 3 main steps [10] (Figure 2.7):

1. Synthesis gas production,
2. Catalytic conversion of synthesis gas,
3. Distillation of raw methanol.

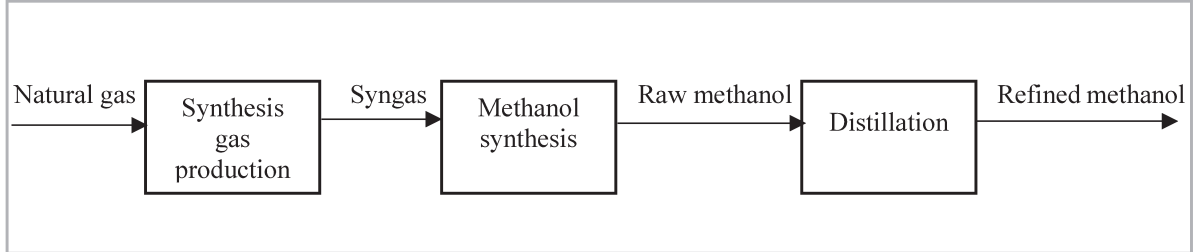
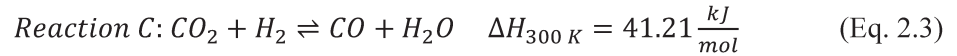
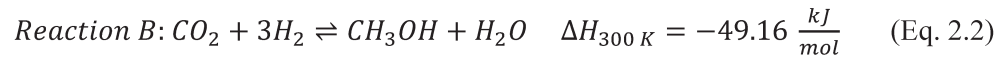


Figure 2.7: Conventional methanol production [12]

The catalytic reaction of syngas can be described by the following three reversible reactions [11]:



As it can be seen Eq. 2.1 and Eq. 2.2 are exothermic, which means that the reaction prefers low temperature, and due to Le Chatelier's principle high-pressure conditions. The maximum conversion is determined by the equilibrium composition. Eq. 2.3 describes the reverse water-gas shift reaction (RWGS), which is mildly endothermic, and links CO and CO₂ together. [9]

The make-up of the syngas is described by the stoichiometric number S, which defines the relation between its compounds, H₂, CO and CO₂ (Eq. 2.4). For the production of methanol, the ideal value of S is 2, or slightly higher. If the value is below 2, which happens if the feedstock for syngas is coal, H₂ should be added to the process, while in case of natural gas feedstock, the value is usually above 2, and around 2.8-3. [10]

$$S = \frac{\text{moles } H_2 - \text{moles } CO_2}{\text{moles } CO + \text{moles } CO_2} \quad (\text{Eq. 2.4})$$

2.3.1.1 Catalysts and reaction conditions used in methanol synthesis

Some of the fabricated and patented catalysts based on the modifications of Cu/ZnO/Al₂O₃ or Cu/ZnO/Cr₂O₃ are listed in Table 2.3. These catalysts produce methanol with selectivity rate above 99.9% [15].

Table 2.3: Overview of some catalysts and reaction conditions used for methanol synthesis from synthesis gas

Company	Components (wt%)				Reaction conditions			Year	Ref
	Cu	Zn	Al	Other	Temperature [°C]	Pressure [bar]	Space velocity		
Shell International Research	40	18	-	Rare earth elements 4	300	53	10 900 h ⁻¹	1971	[9]
Mitsubishi Gas Chemical Company	62	31.5	6.5	-	240	88	30 000 h ⁻¹	2010	[9]
Mitsubishi Gas Chemical Company	57.6	29.5	9.2	Zr 3.7	250	49	4 000 h ⁻¹	1973	[9]
Ammonia Casale	30	50	3	Cr 16	250	100	12 500 h ⁻¹	1982	[9]
Lonza AG	40	20	-	Zr 40	250	50	8 000 l/kg h ⁻¹	1996	[9]
AIST, RITE	45.2	27.1	4.5	Zr 22.6, Si 0.6	250	50	10 000 h ⁻¹	1998	[9]
YKK Corp	76.3	11	12.7	-	250	50	1.7 g/h mol ⁻¹	1998	[9]
Süd Chemie AG	65.2	23.8	11	-	300	100	4 000 h ⁻¹	1984	[9]
Süd Chemie AG	63	27	10	-	250	60	22 000 h ⁻¹	2001	[9]
Süd Chemie AG	65-75	18-23	8-12	-	N/A	N/A	N/A	1987	[11]
IFP	25-80	10-50	4-25	-	N/A	N/A	N/A	1987	[11]
Shell	71	24	-	Rare earth oxide 5	N/A	N/A	N/A	1973	[11]
ICI	61	30	9	-	N/A	N/A	N/A	1965	[11]
BASF	65-75	20-30	5-10	-	N/A	N/A	N/A	1978	[11]
Du Pont	50	19	31	-	N/A	N/A	N/A	1986	[11]
United Catalysts	62	21	17	-	N/A	N/A	N/A	1986	[11]
Haldor Topsøe	37	15	-	Cr 48	N/A	N/A	N/A	1986	[11]

The currently used low-pressure catalysts were first developed by ICI in 1966, which made methanol synthesis more economical. The copper part of the catalyst is considered the main active site of the catalyst; zinc oxide is the stabilizer, while alumina or chromia is used for stabilizing and preventing sintering. [11]

The lifetime of the catalyst depends on the operating conditions, and the impurities in the syngas. Poisoning and sintering are the most common reasons of catalyst deactivation, which leads to increased operating costs. Poisoning is due to impurities in the syngas such as sulphur (above 5 ppm), chlorine, iron and nickel carbonyls, while sintering is caused by increasing temperatures, especially above 270°C. [10] The average lifetime of catalysts is between two to five years [11].

Presently, since the development of low-pressure catalysts, the operating conditions of methanol synthesis processes are temperature between 200 and 300°C, and pressure between 50-100 bar. Even though the equilibrium reactions would prefer lower temperatures, the catalysts are active within this region. [10]

2.3.1.2 Methanol synthesis reactors

The reactor used for methanol synthesis is the most crucial part of the process, as it is not only responsible for the reaction itself, but also for removal of heat generated during the process [38]. Current reactor designs for methanol synthesis are mostly fixed-bed gas phase technologies, which can be either characterized thermodynamically, by cooling type, or by flow design [11]. Fluidized-bed gas phase, liquid phase and membrane based technologies are emerging [10].

Gas phase reactors are either adiabatic or quasi-isothermal. Adiabatic reactors can be quench reactors, consisting of adiabatic multibed quench systems, and adiabatic reactors organised in series with indirect cooling (Figure 2.8). In multibed quench systems (Figure 2.8a), the cooling is done by adding mixture of cooled fresh and recycled syngas between the catalyst beds. [9]

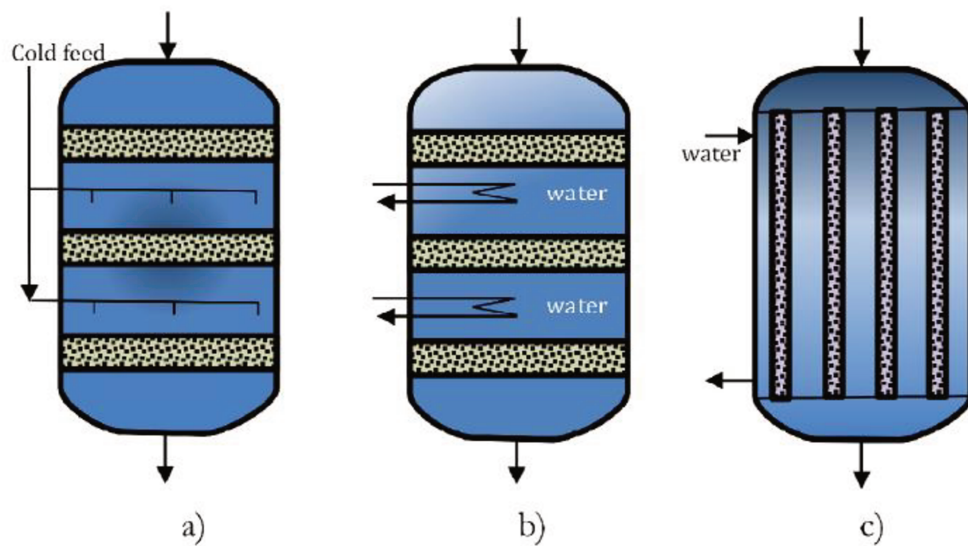


Figure 2.8: a) Adiabatic reactor with direct cooling, i.e. quench reactor; b) adiabatic reactor with indirect heat exchange; c) reactor with external cooling [10]

Even though the quench reactor design is a reliable, simple and the most common design applied in the industry available from Johnson Matthey, it has its disadvantages. There are hot and cold zones within the bed, which means that some parts have low reaction rate due to low temperature for catalyst pellets, while other parts face catalyst deactivation due to too high temperature. Optimizing the reactor is difficult; heat recovery and conversion rate is lower, which leads to higher recycle rates. [10]

In multiple adiabatic reactors, 2-4 vessels are organized in series where the syngas enters the first reactor, and cooling is taken care by intercoolers located between each reactor (Figure

2.8c). The design results in lower operating cost compared to quench converters due to decreased volume of catalyst needed, and lower investment costs. The design is easily scalable up to 10000 t/d or more. [9, 10, 38]

The quasi-isothermal process differs from the adiabatic one in the way of heat removal. In isothermal operation, the average reaction temperature of catalyst bed is lower than in adiabatic reactors, which results in lower amount of by-products and longer catalyst lifetime. Less catalyst is needed to produce the same amount of methanol than in adiabatic converters, which means that isothermal reactors have higher efficiency, expressed by space time yield (STY), than adiabatic ones. [9]

Quasi-isothermal reactors are generally water-cooled, tubular reactors, where the reaction takes place in tubes filled with catalyst. Heat is removed by the boiling water outside the tubes. These kind of reactors operate at milder temperatures, between 240-260°C, however, recycle rates can still be substantial. This kind of reactors have several advantages even though the high investment cost. It carries all the advantages that a quasi-isothermal reactor has, such as good temperature control, catalyst overheating is not possible, start-up and catalyst load changes are easy, and the produced steam can be used for other purposes within the process. [9]

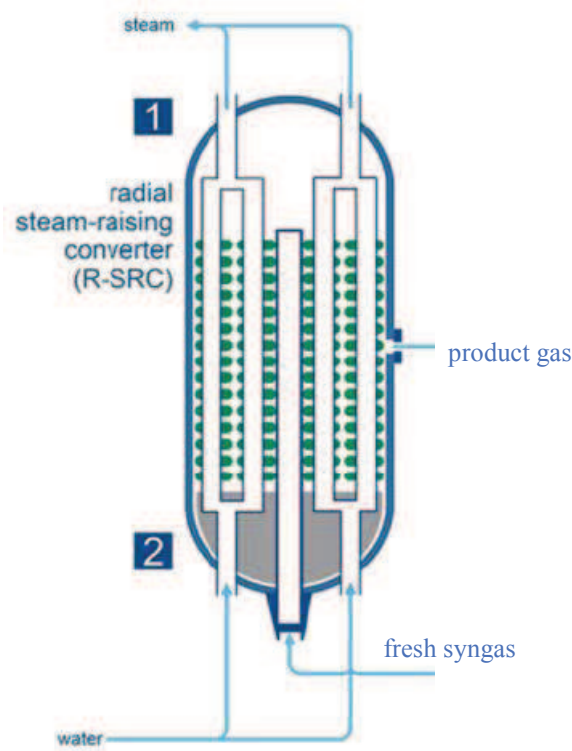


Figure 2.9: Radial water-cooled tubular reactor, Johnson Matthey's DAVY™ [39]

Other quasi-isothermal reactor designs can have the catalyst on the shell side, and the heat can be removed by boiling water or reaction gas (Figure 2.9). Gas-cooled reactors have superior heat removal capacities and close to equilibrium temperatures control. Double-tubular converters, where catalyst is loaded in the annular space between the inner and outer tubes are also cooled by water. [9, 11]

These reactors can be used individually, in series, or in combination with other type of reactors. Such example for a mix of reactor types is Lurgi's process design (Figure 2.10) where a water-cooled reactor is followed by a gas-cooled reactor. Other example is Haldor Topsoe's design where an adiabatic top layer is installed in a boiling water reactor. These combinations lead to more optimal use of the expensive water-boiling unit. [9]

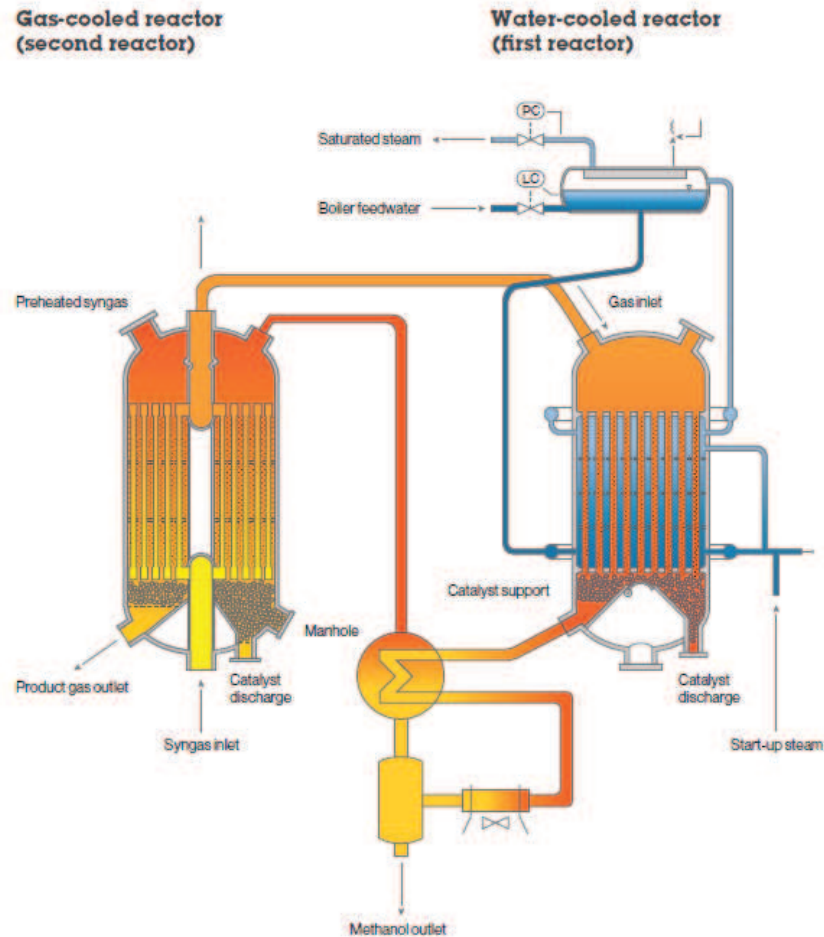


Figure 2.10: Lurgi's two-stage process design [23]

Liquid phase technologies compared to the earlier described fixed-bed reactors employ reactors where the reaction takes place in a liquid from where methanol can be removed. This fluidized-bed also functions as an improved heat removal medium. LPMeOH technology by Air Products uses mineral oil as medium in which commercial methanol catalyst is suspended in powder form (Figure 2.11). The heat is transferred from the mineral oil to boiling water in an internal tubular heat exchanger. This design allows more efficient heat and mass transfer coupled with lower investment and operating cost compared to traditional tubular fixed-bed converters. However, liquid phase technologies are considered more prone to catalyst deactivation than gas phase converters. The design is especially suitable for syngas produced from coal. [10, 38]

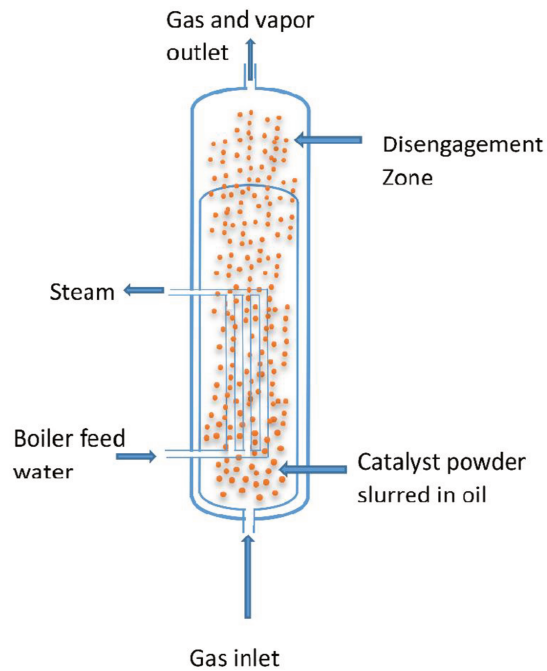


Figure 2.11: LPMeOH slurry reactor [10]

In membrane reactors the reaction and the separation of methanol from water is done in the same vessel, which leads to reductions in investment costs. Advantages of membrane reactors beside low costs are increased yields; however, optimal operating conditions for the catalyst and membrane are conflicting. This is due to the low stability of membranes, which can be increased by lowering the operating temperature and pressure. However, the catalyst is less active at these conditions. [9] Such reactors exist only at lab-scale currently. Other emerging reactor technologies for methanol production from syngas are catalytic distillation process and slurry phase co-current synthesis of methanol process. [38]

The original reactor developed by ICI in 1966 was low-pressure quench reactor with axial flow design. This design is suitable for smaller plants, below 3000 t/d, as the axial flow is a simple and cheap design. Larger reactor sizes led to the development of radial and axial-radial flow designs, as the axial flow is not economical anymore due to the increased pressure drop in large diameters. In current commercial converters, axial, radial, and axial-radial flow designs can be found for both adiabatic and quasi-isothermal reactors. [9]

For methanol plants with a capacity over 3000 t/d it is not enough to simply double the reactor sizes, new synthesis loops and a combination of reactors are necessary to ensure that cost benefits are achieved while the process is kept energy efficient. This way plants with capacities above 5000 t/d, and even 10000 t/d are being built today. [9]

2.3.1.3 Methanol distillation

Crude methanol leaving the flash separator contains beside water low- and high-boiling components. Distillation, in order to improve the purity of methanol, is necessary. For fuel-grade methanol, a single column system is sufficient, while chemical-grade methanol needs multiple column system. The required purity of the end-product methanol has significant effect on the distillation system, as fuel-grade methanol requires lower investment cost, and it consumes one third of the energy necessary for chemical-grade methanol [15]. Distillation

of crude methanol usually happens in a 2-column system, where the first column removes light-end impurities, while the second column removes the high-end impurities (Figure 2.12). A 3-column distillation system is also available from Lurgi, which has higher energy efficiency than the conventional 2-column system, but produces methanol with the same purity. In the energy-saving 3-column configuration, the conventional second, pure methanol column is exchanged for two columns with different pressures. One column operates at elevated pressure, while the other at atmospheric pressure. The atmospheric column reboiler uses the heat from the pressure column overhead vapour, which leads to 35% less energy use for the heating of the combined pure methanol column compared to the conventional single pure methanol column. [9]

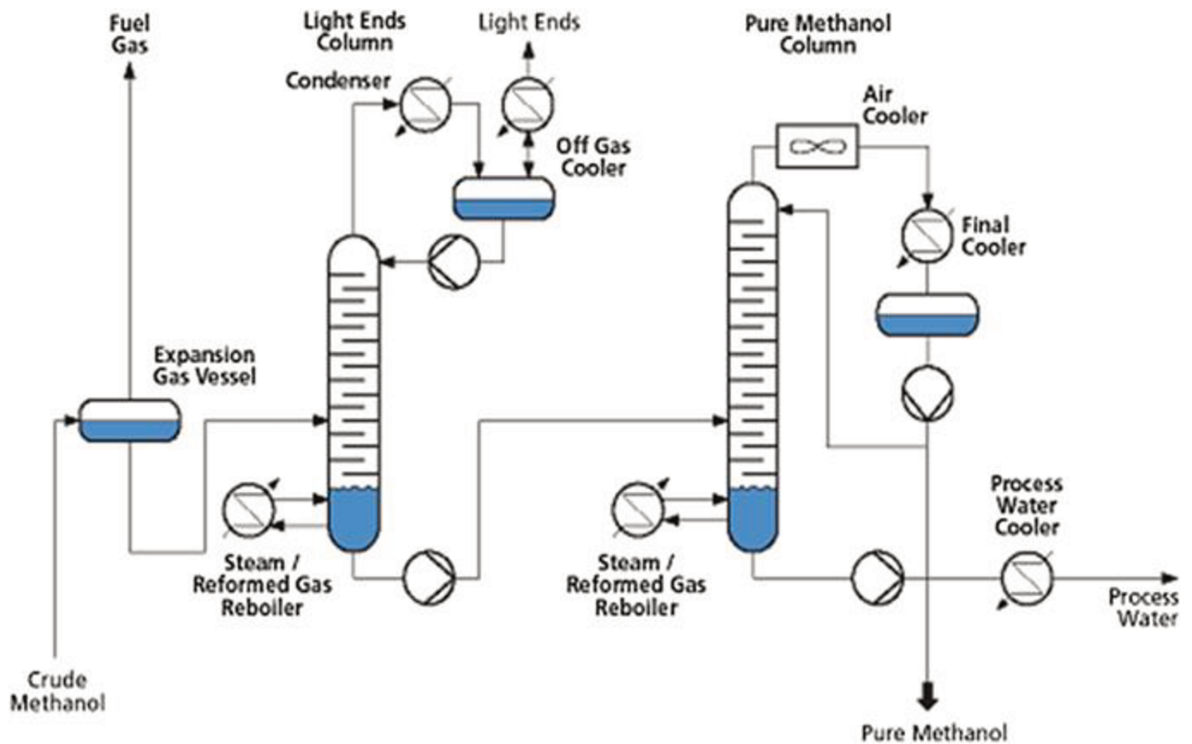


Figure 2.12: Two-column distillation system from Lurgi [9]

The easiest by-product to remove is water, while some components, such as ketones seem to be more difficult, making distillation problematic [40]. After removing water crude methanol contains 1510-1800 ppm by-products and the overall selectivity to methanol without water is 99.82-99.95 wt% [40, 41].

2.3.1.4 Summary of process description of methanol synthesis and distillation

In a conventional methanol synthesis process (Figure 2.13), first the fresh syngas is compressed to the required pressure, between 50-100 bar, and mixed with the compressed recycled gas. At the gas interchanger, the mixed gas is heated up before entering the reactor. In the reactor, the methanol synthesis reaction takes place at 200-300°C. After the reaction has taken place, the gases pass through the gas interchanger, followed by an additional cooler to decrease the gas temperature to 40°C before entering the separator. In the separator, crude methanol is separated from the unreacted gases. Crude methanol is sent further for distillation, while the unreacted gas is recycled. A recycle loop is necessary to increase the

overall conversion rate, as in low-pressure processes the one-pass conversion is around 10%. Before the recycle compressor, a purge is taken from the recycle loop in order to remove nitrogen, methane, and surplus hydrogen. The exact design of the flowsheet depends on the capacity and the feedstock used for the synthesis gas generation. [9-11]

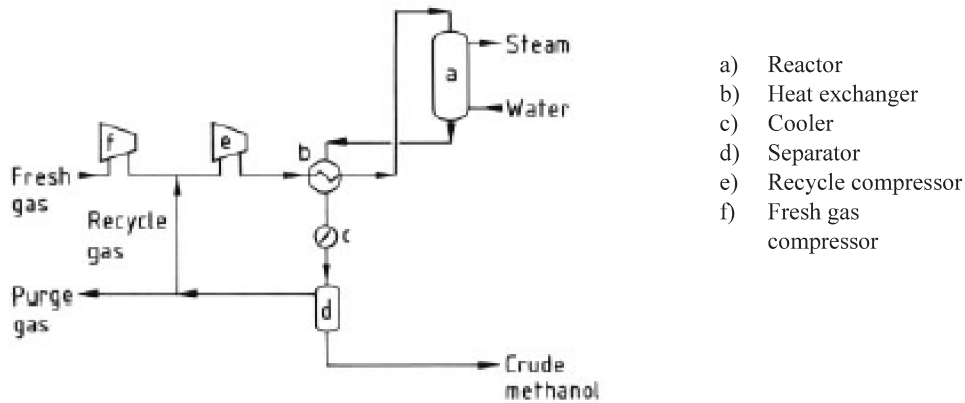


Figure 2.13: Simplified methanol synthesis process [11]

Methanol synthesis plants based on syngas can achieve energy efficiency up to 67-75% and carbon efficiency as high as 83%. [10, 11]

2.3.2 Methanol production via CO₂ hydrogenation

CO₂-based methanol has been investigated as early as the mid-90s, however, it has become the focus of novel methanol production technologies only recently [40]. Due to increasing environmental concerns arising from growing CO₂ emissions, diminishing fossil fuel resources and escalating population and consumption, methanol production from alternative sources seems a viable part of a long-term solution for these problems. Methanol and its derivatives are considered carbon neutral, if the CO₂ is of biogenic origin, and hydrogen is generated by renewable electricity.[9, 40, 42]

Commercialization of methanol synthesis via CO₂ hydrogenation is driven by political and ecological considerations as its main attractiveness is the reduction in CO₂ emissions, which can be achieved only if hydrogen is produced from renewable sources and if clean CO₂ can be produced economically. [10, 40]

It has been an ongoing research topic whether methanol is formed by the hydrogenation of CO or CO₂. CO₂ is considered a less favourable route than CO as it requires more hydrogen and more reaction steps [15]. In the early methanol synthesis plants, CO₂ was completely removed from the process. However, the current molar composition of syngas is CO/CO₂/H₂ (10:10:80) thanks to an accidental discovery of not removing CO₂ from syngas yielded more methanol [43]. Bozzano et al. [10] has collected the works of different authors over a fifty-year period discussing whether CO, CO₂ or both of them is the source of carbon for methanol synthesis. Accordingly, different kinetic models have been developed for the different hypotheses depending on the source of carbon.

2.3.2.1 Catalysts and process conditions used for methanol synthesis from CO₂ and H₂

CO₂-based methanol synthesis follows the same three reversible reactions (Eq.2.1-2.3) as conventional synthesis. Due to these similarities between more CO₂-based and more CO-based methanol synthesis, it is possible to apply the same catalysts for both carbon sources. However, highest productivities can be reached by using catalysts specially designed for CO₂-feedstock. [9, 40]

A pilot plant measurement and simulation conducted by Lurgi, reported by Pontzen et al. [40], was carried out at close to conventional process conditions investigating the behaviour of the conventional methanol synthesis catalyst when only CO₂ and H₂ is used. Productivity (STY) of the process was always higher for CO-based syngas, but optimizing the conditions could make CO₂-based synthesis closer to these results. However, with CO₂ the process is more selective producing 5 times less by-product content, excluding water, due to the lower temperature in the catalyst bed, which results in easier distillation process. Before distillation, the CO process contains 10-12 wt% water, while the CO₂ process 30-40 wt%, meaning that a third of the hydrogen ends up as water by-product. The project has concluded that it is possible to produce methanol by conventional synthesis process, however, commercialization is still a long way ahead.

Doss et al. [44] investigated the performance of a commercial Cu/ZnO/Al₂O₃ catalyst in a fixed-bed reactor under different process conditions. The experiments showed that increasing space velocity results in decreasing CO₂ conversion, while increasing pressure constantly increases it. Maximum methanol yield and carbon conversion was found at 240°C, 124.1 bar and 3300 h⁻¹ space velocity. They advised to decrease the pressure from the optimum to 96.5 bar considering equipment limitations.

Researchers of RITE and NIRE, as described by Saito et al. [45], developed several Cu/ZnO-based ternary and multicomponent catalysts containing different metal oxides specifically for CO₂-feedstock methanol synthesis. The most promising multicomponent catalyst was Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃ where ZrO₂ and Al₂O₃ improve the surface area of copper, while Ga₂O₃ increases the specific activity of the catalyst. The developed catalyst proved to be stable and productive in a pilot-scale plant over a long period when using CO₂ as feedstock. The same catalyst was used in a bench-scale plant producing 50 kg methanol per day [46]. Using the multicomponent catalyst at GHSV 10000 h⁻¹, 250°C and 50 bar the STY was 0.6 kg methanol/(L_{cath}h). The production rate of methanol increased with increasing pressure and reached equilibrium at 270°C. The catalyst proved to be very selective towards methanol and the produced methanol had a purity above 99.9% except water.

In 2000, Ushikoshi et al. [47] reported that their group developed and tested a different multicomponent catalyst, Cu/ZnO/ZrO₂/Al₂O₃/SiO₂. The catalyst behaved similarly under the same conditions as the earlier mentioned multicomponent catalyst and had a 99.7% selectivity towards methanol, except CO and water. The produced crude methanol had a purity above 99.9% at each tested temperature which is higher than that of commercial plants [41]. The catalyst turned out to produce very low concentration of methane, which means that purge is not necessary. Low concentration of higher alcohols and ketones were detected in the crude methanol, which are the most difficult ones to remove. Based on the pilot plant tests an 8000 t/d synthesis plant was designed where a multi-stage indirect cooling and radial flow reactor was equipped from Toyo.

Within the development of the CAMERE process (introduced in detail later), a highly stable and active catalyst was synthesized with composition of Cu/ZnO/ZrO₂/Ga₂O₃ (5:3:1:1) due to the commercial catalysts having low methanol yield without the recycle loop and deactivating faster from the increased amount of water. The catalyst was very active at lower temperatures compared to commercial ones, and produced methanol yield with 15% per pass. [48]

As collected by Jadhav et al. [6] the Cu and ZnO in the catalyst crystallizes faster thanks to the increased water from RWGS resulting in earlier deactivation and sintering of the catalyst.

At fixed pressures production rate reached equilibrium at temperature between 247-257°C and the maximum methanol production was around 247°C for the research done by Toyir et al. [41]. Figure 2.14 shows that above 250°C a Cu/Zn/Al catalyst even though has a higher CO₂ conversion its selectivity towards methanol rapidly decreases [49]. Gallucci et al. [50] has showed that when CO₂ conversion increases methanol selectivity decreases, and concluded that maximising conversion not necessarily results in an increased methanol yield.

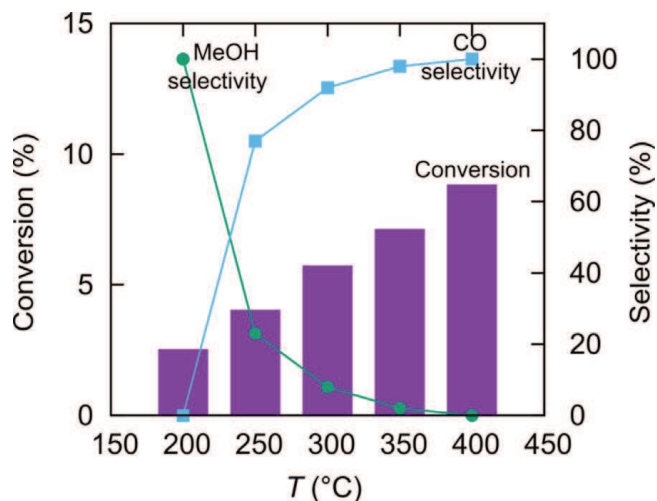


Figure 2.14: Effect of temperature on CO₂ conversion and methanol selectivity over Cu/Zn/Al (50:30:20) catalyst (CO₂:H₂ ratio 1:3, GHSV 2000 h⁻¹ and pressure 20 bar) [49]

Gallucci et al. [50] has also investigated the effect of increasing the H₂/CO₂ feed ratio from 3 to 7 in traditional reactors over commercial catalyst and realized that methanol selectivity was always higher for the higher feed ratio, at 210°C 48% vs 64%. However, this high selectivity comes with higher cost from hydrogen consumption. Ushikoshi et al. [46] noted that CO₂ conversion to methanol decreased with increasing GHSV.

Currently the challenge in CO₂-based methanol synthesis is finding a suitable catalyst; accordingly, several studies and researches focus on these materials. Yet, there is not enough pilot-scale data available, especially ones that study the effects and outcomes of long-term operations. [40] A summary of the listed catalysts can be found in Table 2.4.

Table 2.4: Summary of some of the lab-scale measurements of catalysts and operating conditions for CO₂ hydrogenation for methanol production

Catalyst	H ₂ :O ₂	T [°C]	P [bar]	GHSV [h ⁻¹]	STY [kg/L _{cat} h ⁻¹]	Ref
Standard catalyst Cu/ZnO/Al ₂ O ₃ catalyst (Stüd-Chemie)	3.1	250	80	10500	0.6	[40]
Cu/ZnO/ZrO ₂ /Al ₂ O ₃ /Ga ₂ O ₃	3	250	50	10000	0.6	[46]
Cu/ZnO/ZrO ₂ /Al ₂ O ₃ /SiO ₂	2.82	250	50	10000	0.6	[41]
Standard catalyst Cu/ZnO/Al ₂ O ₃ catalyst (Katalco 51-8)	4	240	69	8500	0.07	[44]

Due to the additional H₂ when CO₂ is used as feedstock for methanol synthesis, the process produces extra water that the distillation system has to be capable of coping with [9, 15]. At the same time, distillation process might be easier compared to conventional methanol as crude methanol from CO₂ does not have ketones [40] (Figure 2.15).

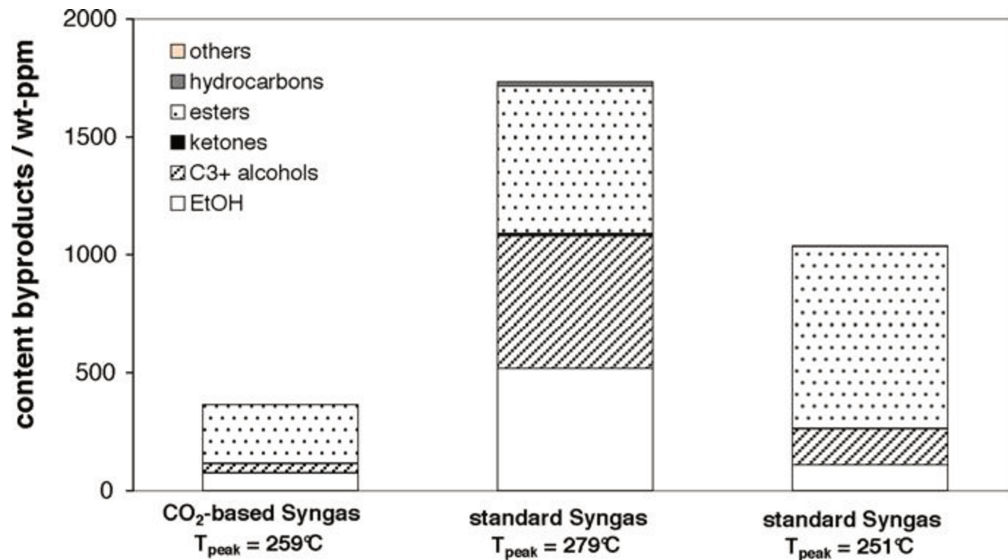


Figure 2.15: Comparison of the by-products in crude MeOH for various feed gas compositions and process conditions [40]

2.3.2.2 Reactors used for methanol synthesis from CO₂ and H₂

According to test measurements reported by Ushikoshi et al. [47] the size difference between the reactor used for methanol synthesis from CO₂ and H₂ and a conventional methanol reactor was negligible. They highly recommend the reactor type provided by Toyo, called MRF-Z due to its excellent temperature control that allows maximum conversion per pass. This reactor is a multi-stage indirect cooling, radial flow reactor that employs bayonet boiler tubes for heat removal.

Gallucci et al. [50] has investigated a zeolite membrane reactor in order to increase methanol yield and selectivity, and CO₂ conversion. A membrane reactor is recommended, as it is capable to remove some of the reaction products in situ thus improving conversion rate. The membrane reactor's performance was compared to a traditional one's using commercial

Cu/ZnO/Al₂O₃ catalyst. The experiments concluded that a membrane reactor has higher methanol yield and selectivity compared to a traditional one at the same operating conditions. Operating temperatures for membrane reactor has to be kept under the critical temperature of methanol, 238°C to keep methanol in vapour phase.

Saeidi et al. [51] has collected the latest research about CO₂ hydrogenation to methanol and concluded that amongst the different factors affecting the CO₂ conversion and product selectivity the reactor type has more crucial role than the type of catalyst or the operating conditions.

2.3.2.3 Economics and environmental aspects of methanol synthesis from CO₂ and H₂

Economic feasibility of producing methanol through CO₂ hydrogenation highly depends on the feedstock prices [40]. According to Goepfert et al. [8] out of the two raw materials hydrogen has a more significant cost effect than CO₂, especially in case if produced via water electrolysis. In case of water electrolysis, 80% of H₂ production cost originates from cost of electricity. They estimated if H₂ is produced at 3 €/kg price then a 5000 t/d methanol plant could produce methanol at 600 €/t production cost.

Galindo Cifre et al. [42] compared studies investigating the production costs of methanol from different feedstock (Figure 2.16) and found that biomass based methanol costs 300-400 €/t, while CO₂-based methanol costs 500-600 €/t. It was found that production of carbon neutral methanol is 2-3 times higher than of fossil methanol. The production cost of methanol via water electrolysis highly depends on the price of electricity.

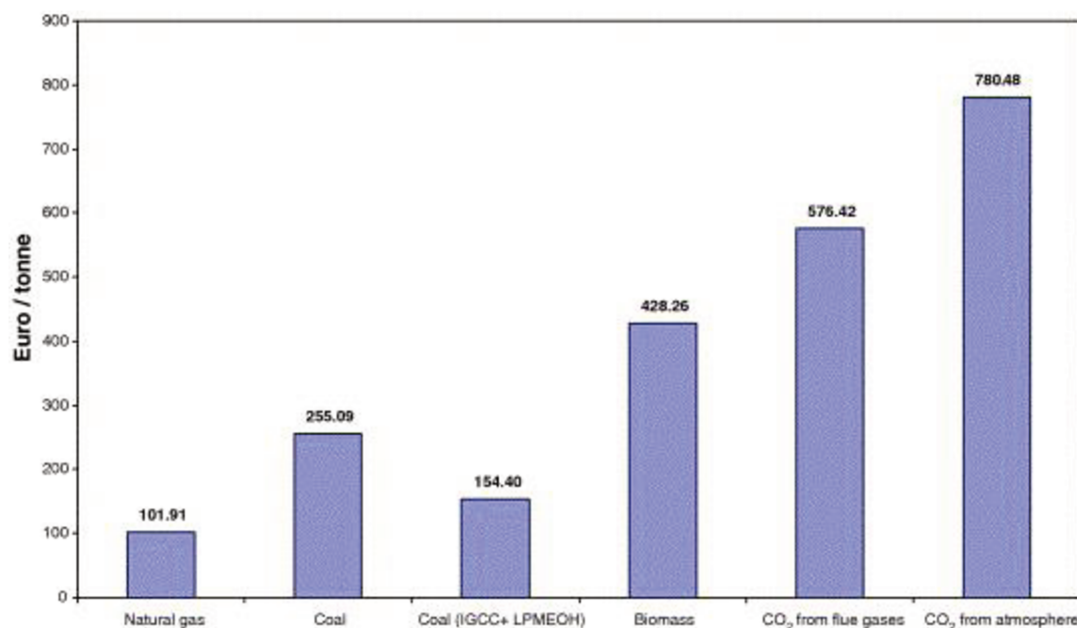


Figure 2.16: Estimated methanol production costs for different concepts of methanol synthesis in 2005 [42]

A summary of reported emissions by Galindo Cifre et al. [42] can be found in Table 2.5. They explained the high CO₂ emissions for CO₂ feedstock originating from flue gases by the energy intensive carbon capture process. 50% of the total emissions were attributed to carbon

capture process. In case of atmospheric CO₂, all processes regarding CO₂ are offset. Regarding energy efficiency, the higher energy demands of CO₂-based methanol processes can be explained as well by the energy intensive separation process.

Table 2.5: CO₂ emissions and energy efficiency of methanol production from different feedstock [42]

	<i>Coal</i>	<i>Natural gas</i>	<i>Biomass</i>	<i>CO₂ from flue gases</i>	<i>CO₂ from atmosphere</i>
<i>CO₂ emission [kg/kg MeOH]</i>	3.8	1.6	0.2	0.8	0.1
<i>Energy efficiency [%]</i>	48.5-61.3	75	51	46	38

2.3.2.4 Existing commercial and pilot methanol plants using CO₂ and H₂

The first CO₂-based methanol pilot plant was developed by Lurgi in 1994, followed by Japanese RITE and NIRE in 1996. The works of Lurgi, RITE and NIRE (now AIST) on the catalyst and the pilot plant have been described above. Since then there are two commercial plants in operation [9].

2.3.2.4.1 Mitsui and RITE

Mitsui Chemicals operates a methanol plant using CO₂ from exhaust gases and hydrogen in Osaka producing 100 t/a methanol [52]. Mitsui's plant operates with the catalyst developed by RITE [53]. They are also working on hydrogen production via photo-catalysis. After the 4500 hours pilot operation the project concluded that it is possible to synthesise methanol from CO₂, and they are currently working on the commercialization and sustainable sources of hydrogen [54].

2.3.2.4.2 CRI

CRI operates in Iceland since 2012 the first commercial methanol plant. Their feedstock is based on CO₂ emissions from a geothermal power plant and H₂ from water electrolysis [55]. Its current production capacity is 4000 t/a methanol, the plant has both electrolyser and CC unit installed with annual capacities of 800 ton H₂ (1200 Nm³/hr) and 5600 ton CO₂ respectively.

2.3.2.4.3 MefCO₂

CRI is currently involved in two pilot-plant projects supported by the EU under Horizon 2020 SPIRE grant, called MefCO₂ and FReSMe. The consortiums include several universities and companies according to the different sub-tasks of the projects. Both projects intend to demonstrate economic and technical feasibility of CCU, namely supplying hydrogen from surplus renewable electricity to CO₂ flue gases. The difference between the two projects is the source of flue gases. The MefCO₂ project will source its CO₂ from an existing coal power plant of RWE in Niederaussem, Germany. Meanwhile in FReSMe CO₂ is captured from a steel production plant's blast furnace. The MefCO₂ pilot plant will produce 1 t/d methanol and will include a CC unit capturing 1.5 t/d CO₂, a 600 kW_{el} PEM electrolyser and a methanol synthetization unit with a newly patented catalyst. A business case study will be conducted based on the pilot plant results for methanol plants with 10000 t and 50000 t annual output. Under FReSMe, the same amount of fuel grade methanol will

be produced, and similar case studies will be conducted. Moreover, the steel plant's behaviour will be studied with the CC unit. [56-59]

Within MefCO₂ four different catalysts, Zn₃O₃/Cu, Cr₃O₃/Cu, Fe₃O₃/Cu and Mg₃O₃/Cu were developed and tested for CO₂-based methanol synthesis [60]. The catalysts' performance was measured by carbon conversion and selectivity towards methanol. The combination of zinc and copper showed the best overall performance for selectivity, stability and activity.

2.3.2.4.4 CAMERE process

Joo et al. [48] developed a two-step CO₂-based methanol synthesis process (carbon dioxide hydrogenation to form methanol via a reverse-watergas-shift reaction, in short CAMERE) and compared it to the conventional fossil one. The two-step process consists of a reactor for RWGS reaction, where CO₂ is reacted with hydrogen to form water and CO, while a second methanol reactor converts the CO, CO₂ and H₂ mix to methanol. Water was removed between the two reactors that led to a decreased recycle gas volume and thus decreased purge gas volume resulting in an increased yield of methanol from 37.01 to 47.87 t/h. Even with the CAMERE process, the limitation stays the same as with the one-step CO₂ methanol synthesis, namely the availability of cheap and fossil free hydrogen.

3 Techno-economic study of a CO₂ hydrogenation methanol plant

In this part of the thesis a simulation of a methanol synthesis plant using hydrogen and CO₂ carried out in Aspen Plus is described. First, a literature review of similar studies will be introduced, followed by the process design and parameters of the current simulation. The simulation focuses on mass and energy balances as well as economic feasibility of the project, and compares two plant setups both having three different yearly methanol output.

3.1 Literature review

Compared to the limited amount of pilot- and lab-scale CO₂-based methanol plants there are several reported models of the process.

Kiss et al. [61] proposed an innovative process to convert CO₂ and wet hydrogen to methanol via a catalytic reactor. The process proved to be highly efficient as a result of a stripping unit leading to the complete recycle of CO₂ and removing the additional water from wet hydrogen. This resulted in minimised utility and raw material consumption. [61]

Van-Dal et al. [62] simulated a methanol plant coupled with a CO₂ capture unit, and investigated the impact of supplying the supplementary steam by combusting some of the CO₂, CO, H₂ and methanol removed from the system. 36% of the thermal energy consumption of the CC process was covered by this supplementary steam. 1.6 ton of CO₂ per ton of methanol was abated if the by-product oxygen from water electrolysis was sold, while it was 1.2 ton if selling of oxygen was not considered. [62]

Abdelaziz et al. [63] constructed three processes for CO₂ hydrogenation to methanol differing in how the flue gases are treated before entering the reactor. The three processes considered are direct use of flue gases without CC, water removal from flue gases, and CO₂ capture. The total cost and CO₂ emission of each process was compared, and it was concluded that while capturing CO₂ prior to introducing it into the reactor had the highest yield, and therefore the shortest payback period. However, this process also emitted most of the CO₂ as CO₂ capture is an energy intensive process, and fossil electricity was considered. The cost of the produced methanol ranged between 230 €/t and 320 €/kg. [63]

Mignard et al. [64] compared four scenarios for methanol production altering in electricity supply when renewable electricity is not available. The steady supply case without oxygen sale was the only scenario that was profitable within the 15-year lifetime of the plant. While if oxygen was sold a second scenario using pressurised electrolysis became also viable. The production cost of methanol ranged between 490 €/t and 760 €/t. [64]

Rivarolo et al. [65] presented two different plant configurations examining how having different source of CO₂, biogas upgrading compared to direct purchase of CO₂, affects the production cost. It was found that the option having on-site CO₂ capture is more economically feasible due to co-selling of bio-methane, even though being more complex and has higher investment cost. When the impact of possible future methanol prices were investigated higher methanol selling prices led to the CO₂ purchasing option become more viable. [65]

Bellotti et al. [66] calculated and compared the profitability of a methanol plant with carbon capture unit for three differing yearly outputs. It was revealed that oxygen sales from the electrolyser are highly beneficial even for larger plants (above 50 kt/a) at methanol market prices point of 600 €/t. Smaller plants (below 10 kt/a) are not economically feasible even with oxygen selling when methanol market price is as high as 500 €/t. As the electrolyser corresponds to around 80% of the investment costs its expected price reduction would significantly decrease the payback period. [66]

Wiesberg et al. [67] explored whether a methanol plant using the process of direct hydrogenation of CO₂ or using indirect conversion of CO₂ via bi-reforming (CO₂ coupling reaction with methane followed by water gas shift reaction) using natural gas is more economical. The direct hydrogenation process turned out to be more competitive, however still non-viable in the Brazilian market with 1120 €/t of hydrogen. Production cost for direct hydrogenation for integrated and non-integrated scenario was 322 €/t and 294 €/t respectively. The cost of hydrogen had a high impact on the feasibility of the process. If natural gas price is as low as on the US market the bi-reforming process could outperform the direct hydrogenation one even with hydrogen prices below 717 €/t. [67]

Pérez-Fortes et al. [68] constructed the model of a methanol plant with carbon capture unit with 440 kt/a output. The most expensive equipment in the plant was the compression system, as hydrogen was sourced from outside of the plant. It was found that the plant under the current market conditions is not viable, only if either the market price of methanol increases to above 720 €/t, or the cost of hydrogen decreases to 1450 €/t, or the plant receives at least 220 € per ton of CO₂ consumed. [68]

These reports all modelled the production of fuel grade methanol. Regarding economic analysis, none of the reports considered the comparison of owning a CC plant with direct purchase of CO₂. This thesis attempts to close this missing gap by providing a detailed description of how to achieve chemical grade methanol in process simulation.

3.2 Methodology

This thesis compares the economic feasibility of a methanol synthesis plant considering three different yearly methanol outputs and two options for CO₂ source. The methanol produced in each case is chemical grade purity. Option I assumes that the methanol plant is operated together with a CC unit, while in Option II CO₂ is considered a purchased raw material. The whole plant is supplied by fossil-free electricity, and CO₂ is captured from flue gases of a biomass boiler. The overview of the process is shown in Figure 3.1.

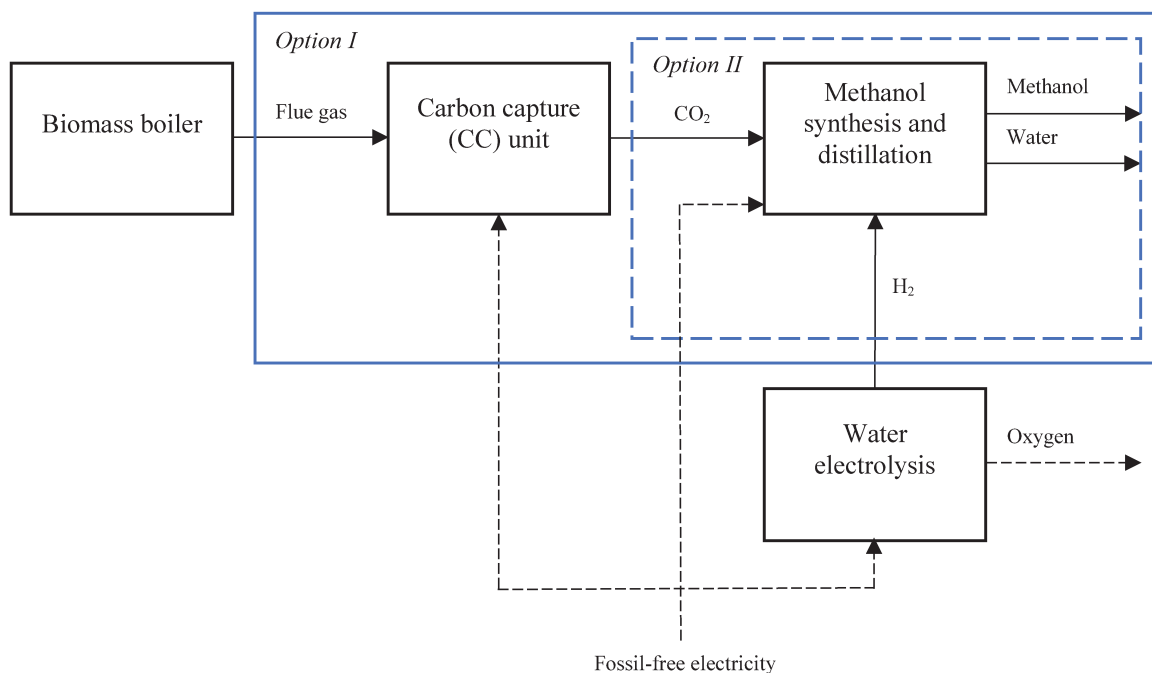


Figure 3.1: Block diagram of the boundary conditions for the simulated cases

Aspen Plus™ V8.8 software was used to simulate the methanol synthesis and distillation plant. The simulation of the electrolysis plant is not included in the thesis, the results were provided by Vattenfall AB. Cost of hydrogen, for the economic part, is considered at levelised cost. This means that the capacity of the methanol plant influences the cost of hydrogen. This method was used as ideally the methanol plant would be built together with a water electrolysis unit. However, it was not in the interest of Vattenfall AB to share the detailed economics behind the electrolysis unit.

The information about consumption parameters of the carbon capture unit were adopted from the simulations done by Onarheim et al. [69]. Stoichiometric feed, CO₂:H₂ 1:3 is used in the processes producing 10 kt/a, 50 kt/a and 250 kt/a methanol. The methanol plant having 50 kt/a output without CO₂ capture unit is considered as base scenario for the thesis.

3.2.1 Water electrolysis unit

Hydrogen was considered to be generated by a typical alkaline electrolyser that uses 51.1 kWh/kg H₂ electricity. For each kilogram of H₂, the electrolyser generates 7.95 kg O₂ that could be sold for other industries, hospitals or fisheries [62, 66].

Figure 3.2 shows the simplified process of water electrolysis. The process uses de-ionized water for the electrolyser, and the whole plant is operated by fossil-free electricity. Hydrogen is dried and then compressed to 50 bar before being sent to the nearby methanol plant.

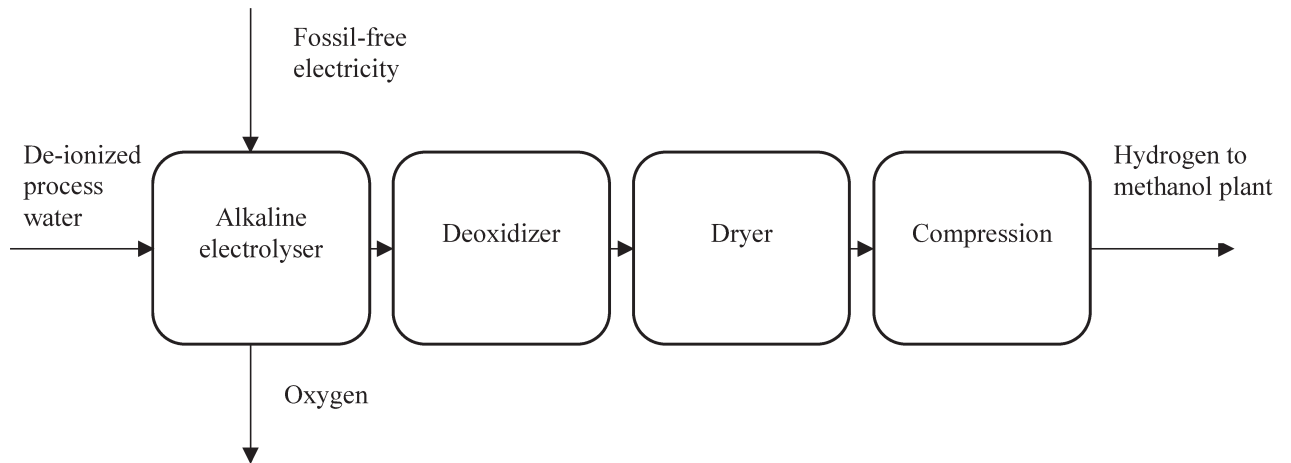


Figure 3.2: Schematic of alkaline electrolysis of water for hydrogen production based on information from Vattenfall AB

3.2.2 Carbon dioxide capture unit

The CO₂ capture unit was not simulated within this thesis, calculations were based on the reported data by Onarheim et al. [69]. The data collected from the simulation included flue gas composition, and utility use, and can be found in Table 3.1. The short description of the process is described below, and the flowsheet can be found in Figure 3.3.

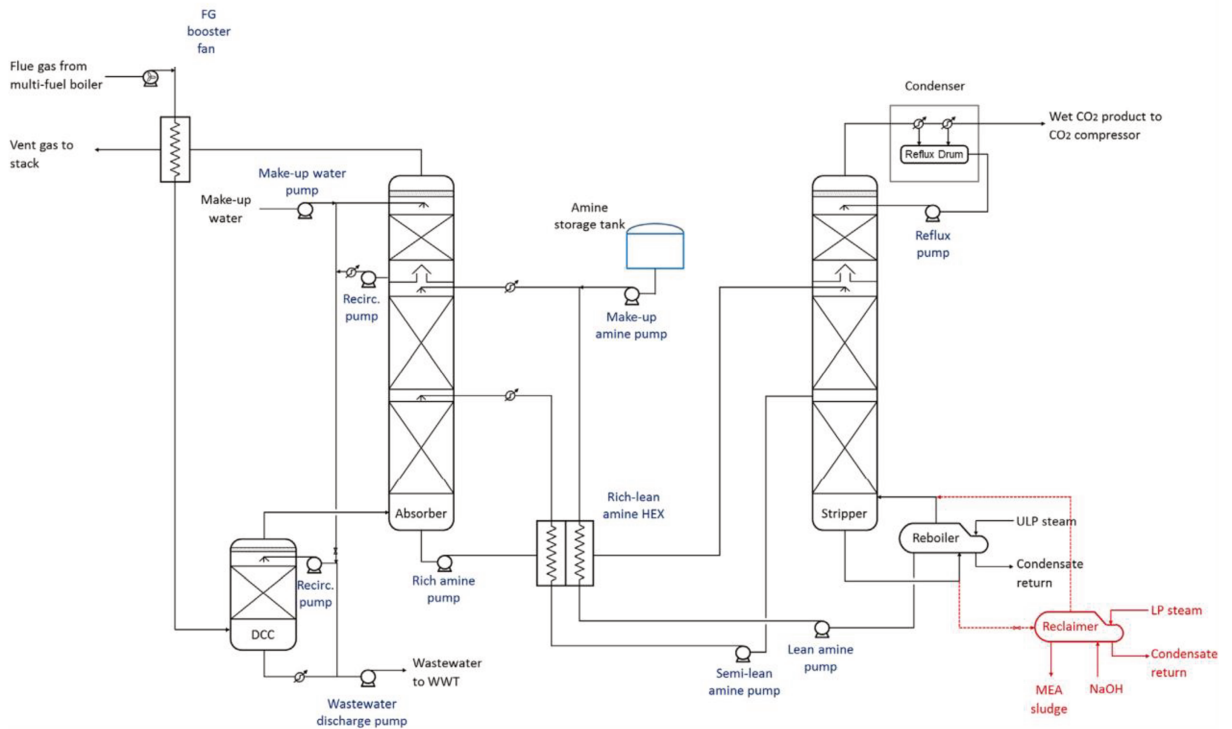


Figure 3.3: Simplified block flow diagram of the post-combustion CO₂ capture plant taken directly from Onarheim et al. [69]

The CC unit mainly consists of two columns: the CO₂ absorber, where CO₂ is absorbed by some kind of amine, in this case 30% MEA solvent, and the stripper, where the amine is regenerated for reuse. Flue gases from a pulp and paper mill's multi-fuel boiler enter the

plant and are preheated by the vented gases leaving the absorber column. Prior to entering the column, the flue gas is quenched and conditioned with cooling water in a direct contact cooler (DCC). Flue gas enters at the bottom of the absorber column where lean and semi-lean amine are injected. Rich amine leaves at the bottom of the column and preheated by the lean and semi-lean amine coming from the stripper. The stripper column consists of a reboiler and a condenser unit. Wet CO₂ leaves on the top of the column and passes through a condenser to remove most of the water. The regenerated lean and semi-lean amine are sent back to the absorber column.

Table 3.1: Performance, energy and utility use of CC unit from multi-fuel boiler by Onarheim et al. [69]

<i>Parameter</i>	<i>Amount</i>	<i>Unit</i>
<i>CO₂ capture</i>	271.00	kt/a
<i>CO₂ content of flue gas</i>	18.98	wt%
<i>Capture efficiency</i>	94.68	%
<i>MEA makeup</i>	1.00	kg/ton CO ₂ captured
<i>Water makeup</i>	416.67	kg/ton CO ₂ captured
<i>Electricity usage</i>	0.14	MWh/ton CO ₂ captured
<i>LP steam usage</i>	1.40	t/ton CO ₂ captured
<i>MP steam usage</i>	6.20	kg/ton CO ₂ captured
<i>Cooling water usage</i>	88.46	kg/ton CO ₂ captured

3.2.3 Methanol synthesis and distillation plant

The simulation of the methanol synthesis and distillation unit of the methanol plant were mostly based on the works of Kiss et al. [61]. The flowsheet of the process constructed for this thesis can be seen in Figure 3.4 and is explained below.

Carbon dioxide is fed at 18 °C and 2 bar from the CC plant, and it is compressed to 50 bar by a series of compressors (COMPR1-4) with intercooling (HX1-3) to 38 °C. Hydrogen enters from the electrolyser at 50 °C and 50 bar. The gases are mixed with the recycled gas (MIXER1) and then heated to 250 °C (HX4). The make-up gas is fed to the isothermal reactor (REACTOR) at 50 bar and 250 °C. The gases leaving the reactor are cooled to 30 °C (HX5) and then separated in a flash separator (SEP1) to liquid raw methanol and non-reacted gases. The non-reacted gases are recycled to the reactor after purging 0.5% (SPLITTER) in order to prevent the accumulation of by-products and inert gases in the system. Raw methanol from the separator is expanded to 1 bar in a flash separator (SEP2) to further remove the non-reacted gases, especially CO₂, and by-products in order to ease the distillation process. Raw methanol is heated to 86.6 °C (HX6) and injected to the first column of the distillation system (DIST). Here, water is separated from methanol, and leaves the column at the bottom. Methanol leaves on the top of the column and enters the second column (RECT). The bottom of the second column is recycled back to the first column as it contains significant amount of methanol beside water. The condensed methanol leaves at the top of the column at 60 °C and it is further cooled (HX7) to 30 °C for storage. Non-reacted gases with some methanol are combusted (BOILER) with the purge stream and vapour stream from flash separator (SEP2) to generate steam. The generated steam is cooled down (HX8) to 120 °C in order to be used within the process or to be sold.

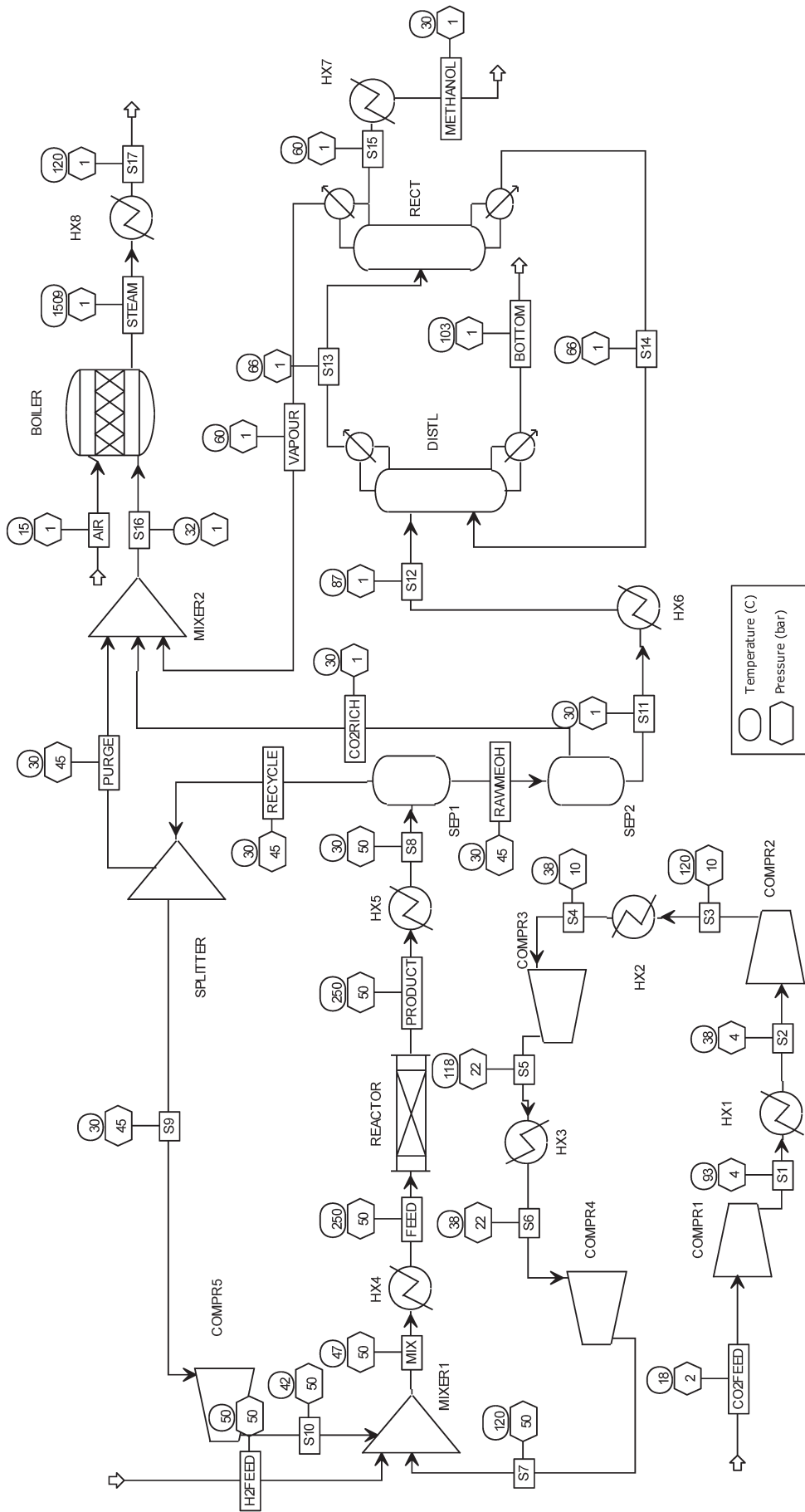


Figure 3.4: Flowsheet of the methanol synthesis plant developed in Aspen Plus, without heat integration

3.2.3.1 General procedure of methanol synthesis simulation

The methanol output of the plant was calculated by using Design spec tool in Aspen. The required methanol output was given in ton/operational year for each size with 0.5 ton/operational year tolerance. From this the tool was required to calculate the necessary mass flow of CO₂ feed stream (CO₂FEED) entering the plant. This was followed by a Calculator tool which was used to calculate the mass flow rate of hydrogen stream (H₂FEED) entering the plant based on the newly calculated CO₂ flow rate. The tool requires a relationship to be indicated between the two parameters. The stoichiometric ratio was used between the two compounds, therefore H₂ = 3×CO₂ (kmol/h) was given for the tool.

The recycle stream to the reactor (S10) was indicated as a tear stream under Convergence/Tear menu point and the amount of maximum iterations was increased from 30 to 500 under Convergence/Options/Methods menu point's Wegstein tab. This was done in order to make the calculations faster, and to avoid error messages, and failed convergence due to mass flow imbalances at MIXER1. [70]

Redlich-Kwong-Soave equation of state (RK-SOAVE) and non-random two-liquid model (NRTL) were used to calculate the thermodynamic properties of high-pressure and low-pressure streams respectively.

3.2.3.2 Kinetic model of methanol synthesis

This thesis used rate equations instead of stoichiometric equations for the synthesis of methanol as a more realistic approach to methanol formation in the reactor.

In this thesis the equilibrium constants from Lim et al. [71], kinetic model from Graaf et al. [72], and experimental kinetic data from An et al. [73] were used as collected and interpreted by Kiss et al. [61] for Aspen Plus. The model considers both CO and CO₂ as the source of carbon for the formation of methanol.

The methanol synthesis in the reactor follows the below rate equations (Eq.3.1-3.3).

$$r_A = r_{CH_3OH,CO} = k_A \frac{K_{CO} [f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / (K_A \sqrt{f_{H_2}})]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_H}) f_{H_2O}]} \quad (\text{Eq. 3.1})$$

$$r_B = r_{CO} = r_{H_2O} = k_B \frac{K_{CO_2} [f_{CO_2} f_{H_2} - f_{H_2O} f_{CO} / K_B]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_H}) f_{H_2O}]} \quad (\text{Eq. 3.2})$$

$$r_C = r_{CH_3OH,CO_2} = k_C \frac{K_{CO_2} [f_{CO_2} f_{H_2}^{3/2} - f_{H_2O} f_{CH_3OH} / (f_{H_2}^{3/2} K_C)]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_H}) f_{H_2O}]} \quad (\text{Eq. 3.3})$$

A kinetic model is used to approximate and simulate how the catalyst works in the reactor. Here a short summary is presented on how to interpret the original article by Kiss et al. [61], and how to introduce the data into Aspen Plus.

Kinetics-based reactions in Aspen Plus can be modelled by application of RPlug type reactors. Aspen Plus offers a generalized Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model. The built-in expression for the LHHW model is in the following format (Eq.3.4):

$$r = \frac{(kinetic\ factor)(driving\ force\ expression)}{(adsorption\ term)} \quad (Eq. 3.4)$$

The rate equation of each reaction (A-C) that happens in the reactor has to be added by giving the kinetic factor, the driving force expression and the adsorption term separately. The reacting phase is vapour, and the basis of reaction rate is catalyst weight for all of them.

The kinetic factor, if T_0 is not specified, can be written as a pre-exponential factor and an Arrhenius-term (Eq.3.5).

$$kinetic\ factor = kT^n e^{-E_a/RT} \quad (Eq. 3.5)$$

In this paper T_0 is not specified, therefore input data from Table 3.2 was used for the reactions.

Table 3.2: Kinetic factor for reactions A, B, C [61]

Reaction	K	n	E_a
A	4.0638×10^{-6}	0	1.1695×10^7 J/kmol
B	9.0421×10^8	0	1.1286×10^8 J/kmol
C	1.5188×10^{-33}	0	2.6601×10^8 J/kmol

The driving force expression is the numerator of the corresponding rate equation. Therefore, it can be written as (Eq.3.6-3.8):

$$Reaction\ A: K_{CO} f_{CO} f_{H_2}^{3/2} - \frac{K_{CO}}{K_A} f_{CH_3OH} f_{H_2}^{-1/2} [Pa^{3/2}] \quad (Eq. 3.6)$$

$$Reaction\ B: K_{CO_2} f_{CO_2} f_{H_2} - \frac{K_{CO_2}}{K_B} f_{H_2O} f_{CO} [Pa] \quad (Eq. 3.7)$$

$$Reaction\ C: K_{CO_2} f_{CO_2} f_{H_2}^{3/2} - \frac{K_{CO_2}}{K_C} f_{H_2O} f_{CH_3OH} [Pa^{3/2}] \quad (Eq. 3.8)$$

As the reacting phase is vapour the difference between fugacity and partial pressure can be neglected, and partial pressure can be used as base of concentration. Aspen requires the driving force to be given in two terms; the first is the positive side of each expression describing the breakdown of reactants, while the second one is the negative side, representing the formation of products. Firstly, the concentration (f) exponent of the components has to be given, followed by the coefficients for the driving force constants (K) given in Table 3.3. K constants are expressed in a logarithmic form (Eq.3.9), hence the coefficients.

$$\ln(K) = A + \frac{B}{T} \quad (Eq. 3.9)$$

Aspen also offers C and D coefficients, which in this case can be written as zero.

Table 3.3: Constants for driving force expressions [61]

Reaction	Term 1		Term 2	
	A	B	A	B
A	-23.20	14225	28.895	2385
B	-22.48	9777	-28.12	15062
C	-22.48	9777	23.974	3222

The adsorption term is the denominator of the rate equations; therefore, it is the same for all three reactions (Eq.3.10):

$$\sqrt{f_{H_2}} + \frac{K_{H_2O}}{\sqrt{K_H}} f_{H_2O} + K_{CO} f_{CO} \sqrt{f_{H_2}} + \frac{K_{CO} K_{H_2O}}{\sqrt{K_H}} f_{CO} f_{H_2O} + K_{CO_2} f_{CO_2} \sqrt{f_{H_2}} + \frac{K_{CO_2} K_{H_2O}}{\sqrt{K_H}} f_{CO_2} f_{H_2O} \quad (\text{Eq. 3.10})$$

The exponent of the adsorption expression is 1 in this case. The adsorption term has to be entered in a two-table format. In the first table (Table 3.4) the concentration (f) exponent is given.

Table 3.4: Exponent for the adsorption term

Component	Term no. 1	Term no. 2	Term no. 3	Term no. 4	Term no. 5	Term no. 6
H_2	1/2	0	1/2	0	1/2	0
H_2O	0	1	0	1	0	1
CO	0	0	1	1	0	0
CO_2	0	0	0	0	1	1

It is followed by entering the coefficients of the adsorption constants (Table 3.5), as K is again expressed in the logarithmic form (Eq. 3.9).

Table 3.5: Constants of the adsorption term

Term no.	1	2	3	4	5	6
Coefficient A	0	-26.1568	-23.2006	-49.3574	-22.4827	-48.6395
Coefficient B	0	13842	14225	28067	9777	23619
Coefficient C	0	0	0	0	0	0
Coefficient D	0	0	0	0	0	0

3.2.3.3 Simulation of methanol synthesis reactor

Aspen Plus offers three different kinds of reactors for such kinetic rate reactions. Plug flow type reactor (RPlug) was chosen, as it is the closest to a real life methanol reactor from the offered types. The chosen RPlug reactor approximates a gas-cooled, tubular reactor. As described earlier these reactors are quasi-isothermal, therefore the operating condition was selected as being constant at the inlet temperature. For the pressure drop Ergun equation was used as suggested by Van-Dal et al. [62]. The diameter of the catalyst was given as 6 mm based on the commercially available catalyst from Haldor Topsoe [74]. The summary of the design parameters for the three differently sized reactors can be found in Table 3.6.

Table 3.6: Design parameters for the reactor of the different methanol plant sizes in Aspen Plus

	10 kt/a	50 kt/a	250 kt/a
Number of tubes	81	405	2025
Length (m)	12	12	12
Diameter (m)	0.06	0.06	0.06
Catalyst loading (kg)	86.5	432.5	2162.5
Bed voidage	0.98	0.98	0.98

3.2.3.4 Simulation of methanol distillation unit

The distillation unit is used to separate the methanol from water, non-reacted gases and by-products. The purity of the final product in this paper was selected to be at least 99.85 wt%, and the distillation column was designed to achieve this target.

The distillation unit was simulated by using the RadFrac unit in Aspen Plus as it provides a more rigorous simulation than the other options. The design is a two-column system where the first column removes water, and the second column removes the non-reacted gases. By-product formation and removal were neglected in the simulation as there is only 500-2000 wt ppm by-product in crude methanol, depending on the feedstock [40]. In real life, by-products would be removed in the second column as well.

The RadFrac unit requires the number of stages, condenser and reboiler type to be chosen. The number of stages were based on the distillation unit designed by Kiss et al. [61]. The reflux ratio, boilup ratio and distillate vapour fraction were tediously examined through sensitivity analysis in order to find the suitable values for the required purity. Besides meeting requirements of purity the losses from both columns were designed to be minimized and the overall heat duty of both columns were kept under a certain limit. A series of sensitivity analysis were performed on the parameters to find the most suitable values that satisfied all the requirements. The final design parameters can be found in Table 3.7.

Table 3.7: Design parameters for the distillation columns in Aspen Plus

	Column #1 (DISTL)	Column #2 (RECT)
Number of stages	30	30
Feed stage	15	15
Recycle stage	1	-
Condenser type	Partial-Vapor	Partial-Vapor-Liquid
Reboiler type	Kettle	Kettle
Reflux ratio (mole based)	1.1	1.1
Boilup ratio (mole based)	0.6	0.8
Pressure (bar)	1	1
Distillate vapour fraction (mass based)	-	0.01

3.2.3.5 Steam generation

Steam is generated from three streams in the plant that either can be used within the process or could be sold. Stream "PURGE", "CO2RICH" and "VAPOUR" were mixed together, this new stream contains (S16, see Appendix 1) mostly CO₂, MeOH, H₂ and CO. Air was introduced to the simulation in order to provide oxygen for the combustion.

The combustion of streams was simulated in Aspen Plus by a stoichiometric reactor (RStoic). This reactor can be used also for reactions when kinetics are unknown. When combustion is selected reactions are not needed to be input. The reactor assumes complete combustion of all compounds that contain hydrogen, carbon, sulphur and nitrogen atoms. Other compounds are ignored. For the combustion product nitrous oxide was selected, while the pressure was left constant and no heat duty was given.

3.2.3.6 Heat exchanger network

Heat integration design was carried out by Aspen Energy Analyser, which applies the Pinch Analysis principles [75] in order to create an energy efficient system by minimizing the use of cold and hot utilities. Pinch Analysis requires the determination of the pinch temperature, which shows where is recoverable heating or cooling duty within the process, and how much utility is needed.

The software extracts stream data from the process design developed in Aspen Plus. Data includes heat duty, heat capacity flowrate (CP), and supply and target temperatures. Aspen Energy Analyser offers different utilities to be used when constructing the heat exchanger network. In this case, cooling water, low-pressure and medium steam generation was chosen as cold utilities, and no heating utility was chosen. The temperature of cooling water was changed from the original 20°C supply temperature to 18°C. Then, the software is capable to recommend certain heat exchanger network possibilities under the given conditions. In this case splitting of streams was forbidden. Once the software has given the recommended designs, the most suitable was chosen. It was decided that the “REACTOR HEAT” is not accepted to have multiple heat exchangers. Finally, the design with the lowest total cost was selected.

3.2.4 Assumptions and calculations for economic analysis

The levelised cost of methanol was calculated by developing a discounted cash flow analysis, and calculating the cumulated net present value (NPV). NPV was set to zero at the end of the lifetime of the plant, and the levelised cost of methanol was calculated from it. A similar approach described by Onarheim et al. [76], called Earnings before interest, taxes, depreciation and amortization (EBITDA) was used in this thesis to calculate the NPV.

No inflation, nor escalation of utilities and raw materials was considered during the economic calculations according to EBITDA. Production capacity was assumed constant during the operational years. General assumptions for the NPV calculations are given in Table 3.8.

Table 3.8: General economic assumptions used in this thesis

<i>Parameter</i>	<i>Value</i>	<i>Comment</i>
<i>Design and construction</i>	3 years	TCI is equally divided
<i>Operational years</i>	20 years	Only annual O&M costs occur
<i>Yearly operating hours</i>	8000 hours	No down-time was assumed
<i>Discount rate</i>	7%	
<i>Reference year</i>	2016	All equipment price was calculated to this year

3.2.4.1 Estimation of total capital investment

The total capital investment (TCI) calculations for the methanol synthesis and distillation unit were based on the estimation of purchased-equipment cost (PEC) for new facilities. TCI was calculated by a simplified relationship between PEC and TCI (Eq. 3.11). TCI includes direct and indirect costs, such as equipment installation, piping, land, civil and architectural work, service facilities, construction costs, and other outlays such as start-up costs, working capital, licensing, R&D. [77]

$$TCI = 6.32 PEC \quad (\text{Eq. 3.11})$$

PEC was taken from Aspen Plus if available. If Aspen did not have available PEC, it was estimated using data from literature. If the size of equipment found in literature differed from the ones in this thesis PEC was estimated by using equation (Eq. 3.12) by Bejan et al. [77].

$$C_{thesis} = C_{literature} \left(\frac{X_{thesis}}{X_{literature}} \right)^\alpha \quad (\text{Eq. 3.12})$$

Moreover, if the cost found in literature was for a different year than the reference year used in this thesis, the original cost was recalculated by using cost index according to Eq.3.13. In this thesis, Chemical Engineering Plant Cost Index (CEPCI) was used. The cost indexes and the exchange rates used are listed in Table 3.9.

$$C_{ref\ year} = C_{original} \left(\frac{I_{original}}{I_{ref\ year}} \right) \quad (\text{Eq. 3.13})$$

The cost of the carbon capture unit was estimated as a whole plant using literature data from Onarheim et al. [76]. The primary design variable characterizing the size of the CC plant is the captured CO₂ annually. A scaling exponent of 0.72 was used according to Bejan et al. [77]. The equation used for the rescaled CC plant can be found in Eq.3.14.

$$C_{CC} = 61.7 \times 10^6 \text{€} \times \left(\frac{CO_{2out}}{2.71 \times 10^6 \text{ton}} \right)^{0.72} \quad (\text{Eq. 3.14})$$

The cost of CC unit calculated this way represents the installed costs only to which contingencies and other CAPEX was added to obtain the total TCI. According to the estimations done by Onarheim et al. [76], the contingency of the plant is 10% of the earlier calculated cost. To this, other 27% is added which covers owner's cost, start-up cost, first fill of MEA, and interest during construction. Equation 3.15 summarizes the TCI calculation of the CC plant.

$$C_{TIC\ CC} = C_{CC} \times 1.1 \times 1.27 \quad (\text{Eq. 3.15})$$

The methanol reactor and the boiler for the methanol plant were calculated based on the report written by Amirkhas et al. [78], where a similar tubular reactor was used. The primary design variable characterizing the size of the methanol reactor was the annual methanol output, while for the boiler it was the heat duty. The scaling exponent was 0.6 for both equipment according to Bejan et al. [77]. Equation 3.16 and 3.17 show how these equipment were calculated for the sizes used in this thesis.

$$C_{MeOHreactor} = 16.39 \times 10^6 \text{USD} \times \left(\frac{MeOH_{out}}{1.71 \times 10^6 \text{ton}} \right)^{0.6} \quad (\text{Eq. 3.16})$$

$$C_{Boiler} = 4.64 \times 10^6 \text{ USD} \times \left(\frac{\text{Heat duty}}{1.71 \times 10^6 \text{ ton}} \right)^{0.6} \quad (\text{Eq. 3.17})$$

After having calculated the cost of rescaled equipment both equipment costs were exchanged from USD to EUR according to CEPCI's exchange rate. To obtain the final PEC for the reactor and the boiler the cost indexes from CEPCI were used to update the prices from 2006 to 2016. [79]

PEC was not available from Aspen for the mixers in the methanol plant, therefore they were neglected, as their cost is insignificant compared to the whole TCI of the plant. For all other equipment PEC was available from Aspen. PEC first had to be converted from USD to EUR followed by updating it by the cost index from 2014 to 2016 as Aspen Plus V8.8 uses prices in USD from year 2014.

Table 3.9: Exchange rates and cost indexes used from CEPCI [79]

Exchange rate USD to EUR		Cost index		
2006	2014	2006	2014	2016
0.7967	0.7536	499.6	576.1	541.7

3.2.4.2 Estimation of fixed and variable operation and maintenance costs

Fixed and variable costs are assumed to occur annually during the operational years. Within fixed cost direct labour costs, administration and general overhead costs, annual O&M costs, insurance and local taxes and fees were assumed to occur.

The amount of personnel, can be seen in Table 10, was estimated based on similar calculations done by Collodi et al. [80].

Table 3.10: Amount of personnel for the different methanol plants

10 kt/a	50 kt/a	250 kt/a	10 kt/a with CC	50 kt/a with CC	250 kt/a with CC
10	12	18	15	17	23

Some of the fixed OPEX depend on the fixed-capital investment (FCI), which can be calculated from TCI according to Eq.3.18. [77]:

$$TCI = 1.47 FCI \quad (\text{Eq. 3.18})$$

Regarding variable costs raw material costs, utility costs, process water, methanol catalyst, and MEA were assumed. Transportation, wastewater treatment, waste disposal and storage costs were not assumed. The summary of the occurring fixed and variable costs can be found in Table 3.11.

For hydrogen cost a levelised cost was applied, which was calculated by Vattenfall AB. CAPEX of electrolyser was assumed to grow linearly, i.e. economics of scale were not taken into account.

CO₂ costs occurred only when CO₂ was bought. When a CC plant was directly attached and owned together with the methanol plant costs arising from the process were used for calculations.

Table 3.11: Fixed and variable operation and maintenance costs

<i>FIXED O&M</i>	<i>Cost</i>	<i>Unit</i>	<i>Comment</i>
<i>Direct labour cost</i>	60000	€/a/person	[80]
<i>Admin and general overhead cost</i>	18000	€/a/person	30% of direct labour cost [80]
<i>Annual O&M</i>	1.5 % of FCI		[80]
<i>Insurance</i>	0.5 % of FCI		[80]
<i>Local taxes and fees</i>	0.5 % of FCI		[80]
<i>VARIABLE O&M</i>			
<i>CO₂</i>	50	€/t	[15]
<i>H₂ for 10 kt/a plant</i>	3.12	€/kg	at 30 €/MWh electricity price
<i>H₂ for 50 kt/a plant</i>	2.74	€/kg	at 30 €/MWh electricity price
<i>H₂ for 250 kt/a plant</i>	2.65	€/kg	at 30 €/MWh electricity price
<i>Electricity</i>	30	€/MWh	Provided by Vattenfall AB
<i>Cooling water</i>	0.05	€/m ³	Provided by Vattenfall AB
<i>Steam</i>	0.015	€/kg	[77]
<i>Process water</i>	2.00	€/m ³	Provided by Vattenfall AB
<i>Methanol synthesis catalyst</i>	8.77	€/kg	Changed every 3 years [67]
<i>MEA solvent</i>	1.62	€/kg	[76]

4 Results

4.1 Technical performance

Table 4.1 shows key performance indicators for easier understanding of the process results. All three plants operate identically, which was achieved changing only reactor size and catalyst loading according to the increase in the yearly output. The desired chemical grade purity was achieved after distillation for each plant size. Consumption of raw materials are close to the stoichiometric values, only exceeding it by 4 and 6 wt% for CO₂ and H₂ respectively.

Table 4.1: Key performance data and comparison of the methanol plants

	10 kt/a	50 kt/a	250 kt/a	Unit
Methanol output	10000.29	50000.07	249999.57	ton/year
CO ₂ usage	1.4	1.4	1.4	ton/ton MeOH
H ₂ usage	0.2	0.2	0.2	ton/ton MeOH
Recycle to feed ratio	4.8	4.8	4.8	mol/mol
H ₂ :CO ₂ at reactor inlet	5.8	5.8	5.8	mol/mol
CO ₂ conversion per pass	29.1	29.1	29.0	mol %
Overall CO ₂ conversion	96.19	96.14	96.19	mol %
Methanol purity	99.87	99.88	99.87	wt%
Steam usage (after heat optimization)	0	0	0	ton/MeOH
Cooling water (after heat optimization)	272.1	272.6	272.1	ton/ton MeOH
Electricity usage	174	174	174	kWh/ton MeOH

Detailed stream tables containing mass balance information are available for all methanol plant capacities in Appendix 1.

Compared to other similar simulations the overall CO₂ conversion rate is acceptable, however, it could be improved with the optimization of the process (Table 4.2). One main point in order to achieve higher overall CO₂ conversion rate is to decrease the amount of purge from 0.5% to 0.1%.

Table 4.2: Comparison of overall CO₂ conversion of similar methanol plant simulations

	<i>This paper</i>	[61]	[62]	[63]	[64]	[67]	[68]
CO ₂ conversion (mol %)	96.19	99.78	92.56	99.74	99.38	97.67	94

4.1.1 Results of heat optimization

The extracted data from Aspen Plus can be found in Table 4.3, where the stream names are assigned by the heat exchanger that they pass through. Beside the material streams, the reactor heat was also extracted, as it requires cooling. Hot streams are process streams that require cooling, while cold streams require heating. Stream data for the other two plant sizes can be found in Appendix 2.

Table 4.3: Stream data of 50 kt/a plant extracted from Aspen Plus for heat integration

<i>Stream</i>	<i>Stream type</i>	<i>Supply temperature [°C]</i>	<i>Target temperature [°C]</i>	<i>Duty [MW]</i>	<i>CP [kW/°C]</i>
<i>HX1</i>	Hot	93	38	0.1	2.3
<i>HX2</i>	Hot	119.7	38	0.2	2.3
<i>HX3</i>	Hot	118.2	38	0.2	2.5
<i>HX4</i>	Cold	46.5	250	8.4	41.5
<i>HX5</i>	Hot	250	30	13.3	342.2
<i>HX6</i>	Cold	30.3	86.8	5.0	706.6
<i>HX7</i>	Hot	60.4	30	0.2	6.6
<i>REBOILER at DISTL</i>	Cold	102.5	103	1.4	2831.5
<i>REBOILER at RECT</i>	Cold	65.7	66.3	1	5205.5
<i>CONDENSER at DISTL</i>	Hot	67.9	66.4	2.6	7062.2
<i>CONDENSER at RECT</i>	Hot	64.4	60.4	4.4	34983.6
<i>REACTOR HEAT</i>	Hot	250	249.5	3.3	6558.5
<i>HX8</i>	Hot	1509.3	120	1.5	3.2

The 50 kt/a methanol plant needs 24.3 MW cooling utility, and 15.9 MW hot utility. HX8 stream was not included in this calculation, as it does not belong to the methanol plant; its sole purpose is to generate steam to be used within the plant, if possible.

Once the streams have been extracted Aspen Energy Analyzer creates the so-called Composite Curves to identify the pinch temperature for the given minimum temperature difference. In this case, 10°C was chosen as the minimum temperature difference. All hot streams are represented by a single hot curve, and cold streams by a single cold curve, together they are called the Composite Curves as shown in Appendix 3 (Figure A1). Where the minimum temperature difference is found between the hot and cold curve that is where the pinch temperature is located. The system is then divided to below and above the pinch areas. Below the pinch is where heat input is required, while above the pinch is where cooling is needed. Where the two curves overlap heat recovery is possible. [75]

As there are several utilities available to choose from constructing the Grand Composite Curve is a necessary tool. The Composite Curves are not suitable when multiple cooling and heating duty are offered, as the curves would have to be reconstructed every time a utility is added [75]. The Grand Composite Curve, see Appendix 3 (Figure A2), shows where is heat integration in the process, and whether and how much excess energy is available.

The chosen optimized heat exchanger design for 50 kt/a methanol plant can be seen in Appendix 4 (Figure A4). The detailed characteristics of the new heat exchangers can be found in more detail in Appendix 4 and 5, including results for the other two plants as well.

For the 50 kt/a plant compared to the original process using 24.32 MW cooling utility, and 15.88 MW hot utility, the integrated process uses only 9.9 MW cooling duty in the form of 1704 t/h cooling water and no heating duty.

Overall more than 75% utility saving was achieved for each plant (Table 4.4). Hot utility need was completely eliminated due to the steam generation within the methanol plant from the boiler.

Table 4.4: Utility need of methanol plants before and after heat integration

	10 kt/a	50 kt/a	250 kt/a
<i>Original hot utility</i>	3.2 MW	15.9 MW	79.4 MW
<i>Original cold utility</i>	4.9 MW	24.3 MW	121.5 MW
<i>Total original utility</i>	8.0 MW	40.2 MW	200.9 MW
<i>Integrated hot utility</i>	0 MW	0 MW	0 MW
<i>Integrated cold utility</i>	2.0 MW	9.9 MW	49.4 MW
<i>Total integrated utility</i>	2.0 MW	9.9	49.4 MW
<i>Cold utility saving</i>	59.36 %	59.3 %	59.4 %
<i>Hot utility saving</i>	100 %	100 %	100 %
<i>Total utility saving</i>	75.4 %	75.4 %	75.4 %
<i>Cooling water usage</i>	340.1 ton/h	1703.7 ton/h	8502.4 ton/h

Table 4.5 shows annual mass flows, annual raw material, and utility use after heat integration for the different plant sizes.

Table 4.5: Annual mass flows, raw material and utility usage after heat integration for the different plant sizes

		10 kt/a	50 kt/a	250 kt/a
<i>Electrolyser</i>	<i>H₂ out [kt/a]</i>	2	10	49
	<i>O₂ out [kt/a]</i>	16	78	390
<i>CC unit</i>	<i>Flue gas in [kt/a]</i>	95	477	2382
	<i>CO₂ out [kt]</i>	14	71	357
	<i>MEA [t]</i>	14	71	357
	<i>Process water [m³]</i>	5949	29762	148737
	<i>Steam [ton]</i>	109	543	2713
	<i>Cooling water [m³]</i>	1263	6319	31577
	<i>Electricity [MWh]</i>	1999.03	10000.17	49975.52
<i>Methanol plant</i>	<i>MeOH out [kt]</i>	10	50	250
	<i>H₂ [ton]</i>	1962	9816	49053
	<i>Cooling water [m³]</i>	2721133	13629400	68018800
	<i>Electricity [MWh]</i>	1.74	8.69	43.41

4.2 Economic results

The final calculated PEC, and total TIC for the equipment of the methanol plant and the CC plant can be found in Table 4.6.

Table 4.6: Total capital investment (TCI) for the CC unit and methanol plant of different sizes with detailed equipment cost, in 2016 million €

<i>Equipment name</i>	<i>10 kt/a</i>	<i>50 kt/a</i>	<i>250 kt/a</i>
<i>Reactor</i>	0.65	1.70	4.47
<i>Distillation columns</i>	0.28	0.43	1.03
<i>Heat exchanger network</i>	0.24	0.56	2.01
<i>Flash separators</i>	0.03	0.04	0.09
<i>Compressors</i>	2.32	2.76	3.81
<i>Boiler</i>	0.04	0.13	0.46
<i>TOTAL MeOH PLANT (PEC)</i>	3.55	5.63	11.88
<i>TOTAL MeOH PLANT (TCI)</i>	22.42	35.58	75.06
<i>CC unit</i>	7.01	22.33	71.12
<i>CC unit TCI</i>	9.79	31.19	99.35
<i>TOTAL MeOH+CC (TCI)</i>	32.21	66.77	174.41

The effect of economics of scale is clearly visible from Table 4.6 for both the methanol plant and the CC unit. The largest methanol plant with CC unit has a TCI less than 5.5 times of the smallest one while its capacity is 25 times more.

Based on the estimated OPEX for the plants in Appendix 6 Figure 4.1 shows that out of the two option for the 50 kt/a plant size the plant with CC unit has lower yearly OPEX. This is explained by the negligible cost effect of electricity, process water and MEA compared to the direct cost of CO₂ buying. From the figure it is also worth to notice that in case of methanol plant without CC around 80% of annual OPEX arises from hydrogen costs, while for methanol plant with CC this reaches close to 90%.

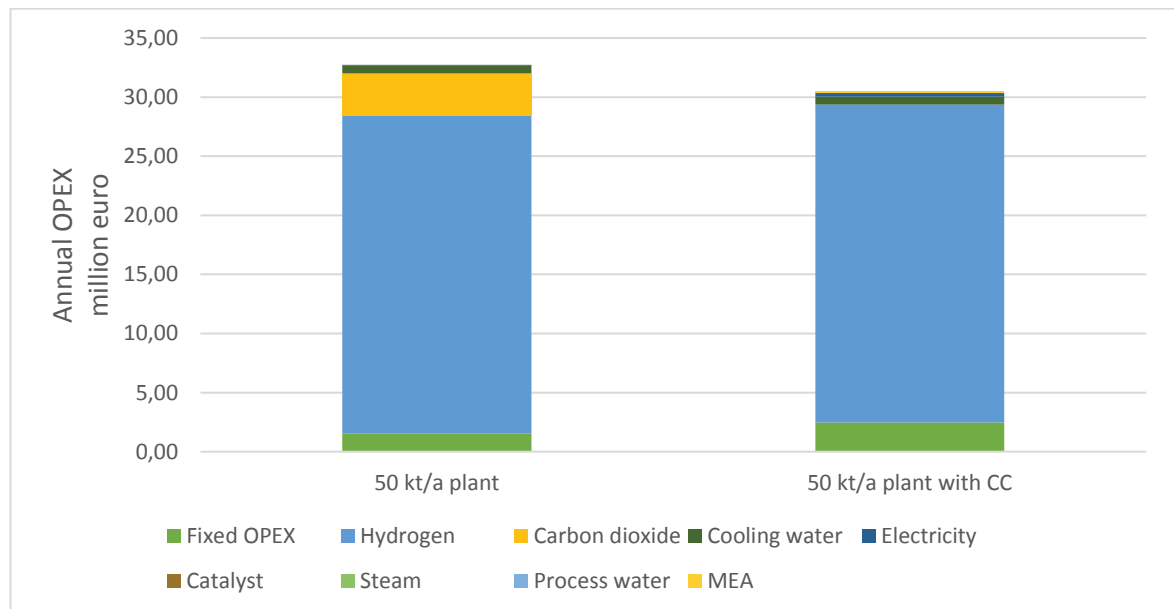


Figure 4.1: Annual OPEX of 50 kt/a plant without and with CC plant

The overwhelming share of hydrogen cost within OPEX can be seen better in Figure 4.2 where all sizes of methanol plant are illustrated.

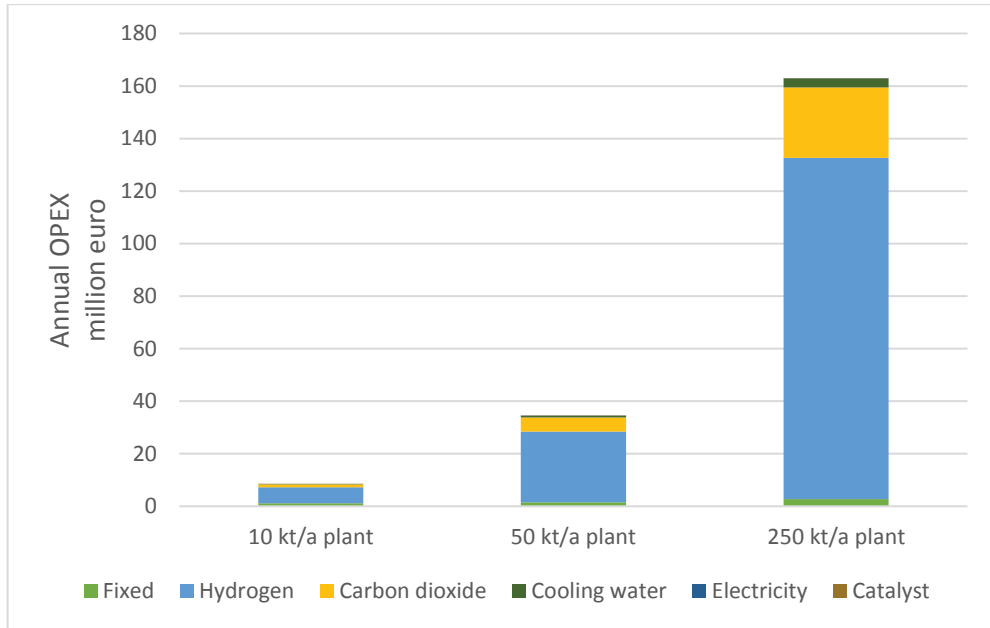


Figure 4.2: Annual OPEX of methanol plants without CC unit

The levelised cost of methanol for the different plant sizes and setups is summarized in Table 4.7. In Figure 4.3 the share of CAPEX and OPEX, influencing the LCOMeOH can be seen as well.

Table 4.7: LCOMeOH for different methanol plant sizes with and without CC unit, €/ton

	10 kt/a	50 kt/a	250 kt/a	10 kt/a with CC	50 kt/a with CC	250 kt/a with CC
<i>LCOMeOH</i>	1035	724	645	1126	743	631

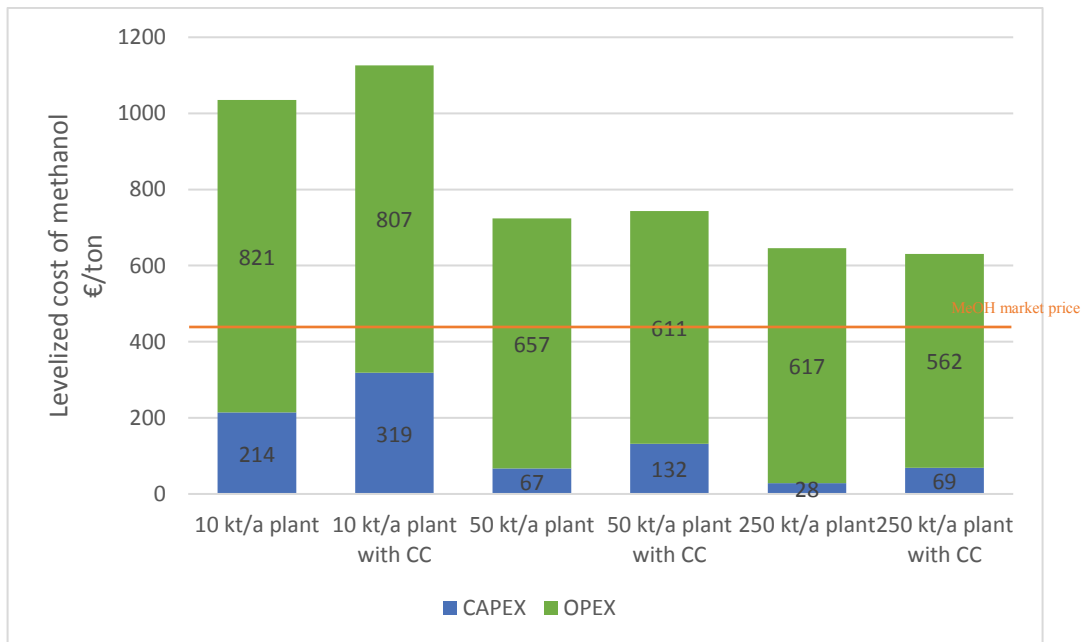


Figure 4.3: Levelized cost of methanol and the effect of CAPEX and OPEX

LCO_{MeOH} as expected decreases significantly with the increasing yearly output, and it ranges between 1130 and 630 €/t. In all cases the estimated LCO_{MeOH} is above the current fossil methanol European market price posted by Methanex [29]. The estimated LCO_{MeOH} is somewhat higher than the earlier estimates by IRENA [37] and Galindo Cifre et al. [42]. However, the findings in this thesis agree that hydrogen cost has the biggest influence on the final LCO_{MeOH}. For the 250 kt/a plant without CC unit OPEX represents close to 90% share of the total LCO_{MeOH} out of which 80% is hydrogen cost. Therefore, more than 70% of this fossil-free methanol production method is associated with H₂ costs.

4.2.1 Sensitivity analysis

Three cost parameters were investigated to see how their behaviour influences the LCO_{MeOH}. Table 4.8 lists the parameters with their original and changed values. Sale of oxygen is not considered when sensitivity of cost of electricity and CO₂ are investigated.

Table 4.8: Cost parameters and their values for sensitivity analysis

<i>Parameter 1 – Oxygen selling</i>		<i>Parameter 2 – Cost of electricity</i>			<i>Parameter 3 – Cost of CO₂</i>		
Option A	Option B	Option A	Option B	Option C	Option A	Option B	Option C
Oxygen is sold at 100 €/t	Oxygen is not sold	20 €/MWh	30 €/MWh	40 €/MWh	25 €/t	50 €/t	75 €/t

When the cost of electricity was changed, also the cost of hydrogen was changed. The levelised cost of H₂ for each plant size and electricity cost can be found in Table 4.9. As mentioned earlier levelised cost of H₂ (LCOH₂) is used as ideally the electrolyser unit would be owned together with the methanol plant, and capacity of the methanol plant would influence the LCOH₂.

Table 4.9: LCOH₂ depending on cost of electricity and size of methanol plant, €/kg H₂

<i>LCOH₂</i>	<i>10 kt/a</i>	<i>50 kt/a</i>	<i>250 kt/a</i>
<i>20 €/MWh</i>	2.55	2.19	2.10
<i>30 €/MWh</i>	3.12	2.74	2.65
<i>40 €/MWh</i>	3.70	3.29	3.18

Figure 4.4 shows how LCO_{MeOH} changes when oxygen, the by-product from H₂ production is sold. For the largest plant with CC unit the estimated LCO_{MeOH} is less than 60 €/t more than the current market price. In all cases significant reduction, around 156 €/t, can be noticed, therefore, considering selling by-product O₂ is a viable option to achieve a better business case.

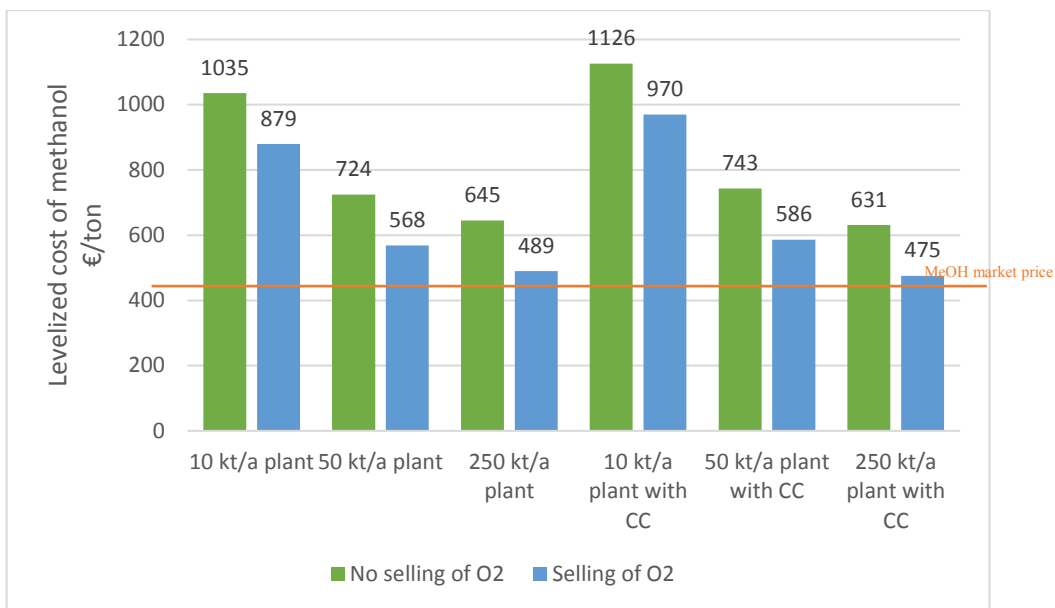


Figure 4.4: Influence of oxygen selling option on levelised cost of methanol

In the second cost parameter change, cost of electricity and the resulting LCOH₂, for a 10 €/MWh change in electricity LCOMeOH changes with around 110 €/t (Figure 4.5). This means that a 10 €/MWh electricity price could make methanol production from CO₂ and H₂ competitive with fossil methanol.

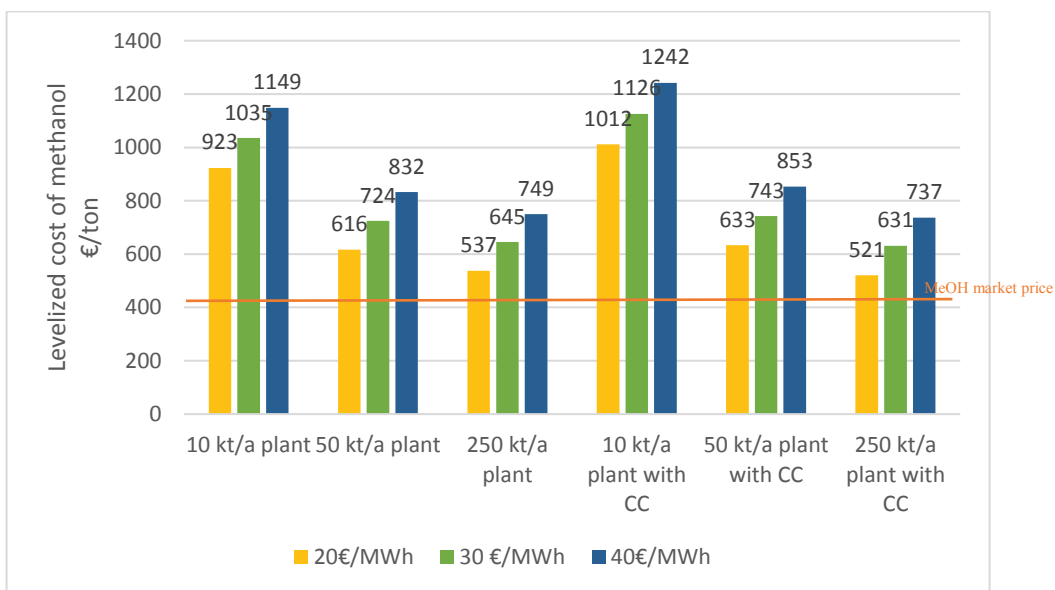


Figure 4.5: Comparison of levelised cost of methanol for differently sized plants with different electricity prices

The last cost parameter, cost of CO₂, has a less significant effect than the other two parameters (Figure 4.6). For a 25 €/t change LCOMeOH changes only by around 35 €/t, which can be understood from the considerable difference in the raw material prices of CO₂ and H₂.

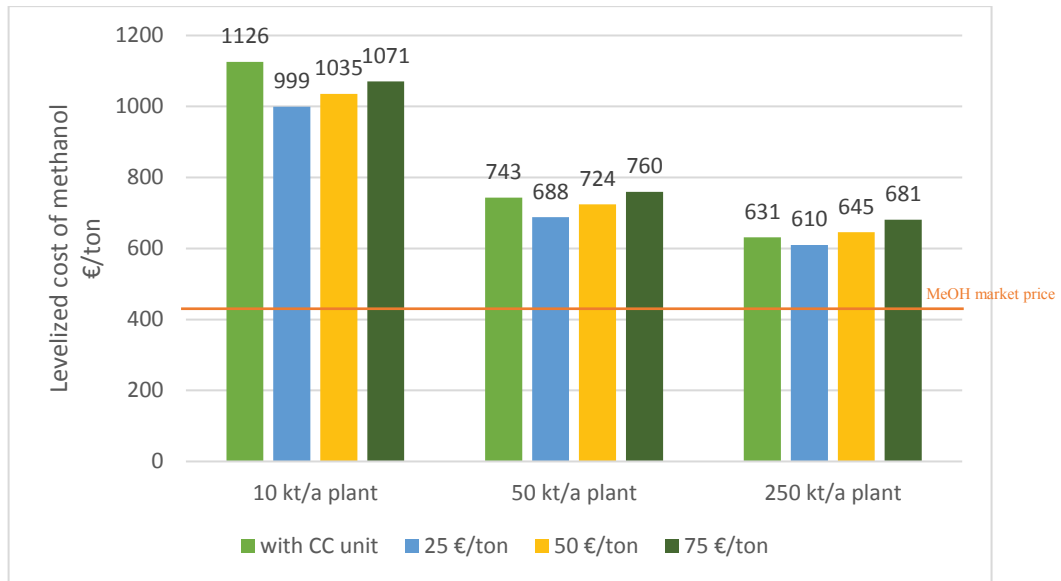


Figure 4.6: Comparison of levelised cost of methanol for differently sized plants with different CO₂ prices and sources

Owning a CC plant becomes beneficial from middle sized methanol plants when the expected market price of CO₂ is higher than 70 €/t. For larger plants it is already a more beneficial investment to own a CC plant when the expected CO₂ market price is as low as 40 €/t. However, for smaller plants it is more profitable to purchase CO₂ even when market prices are over 108 €/t.

5 Conclusion

In this thesis, the production of fossil-free methanol from CO₂ and H₂ was investigated. Methanol is a versatile, globally traded chemical that can serve as energy and hydrogen carrier, and it is a base chemical for the chemical industry. End-products ranging from plastics, textiles, solvents and paints all encounter methanol during their production chain. Emerging technologies in the petrochemical industry, such as MTO, MTG and MTP will be significantly contributing to its forecasted 90 million global demand by 2020.

Currently methanol is almost solely produced from fossil feedstock, mostly natural gas. Analysis and comparison of conventional methanol synthesis and distillation to CO₂ and H₂ based methanol production revealed that while conventional process is a technologically more mature and economical process the fossil-free method is an environmentally better option. CO₂ emissions can be significantly decreased if CO₂-based methanol utilizes renewable energy for both water electrolysis and CC plant operation. It is also a beneficial process in CO₂ mitigation utilizing CO₂ instead of controversial CCS.

Research is still ongoing about the optimization of the CO₂-based methanol synthesis with significant focus on developing suitable, specifically tailored catalysts. However, there is an unfortunate lack of long-term pilot-scale measurements. Based on the present research publications it can be concluded that methanol synthesis from CO₂ and H₂ can be effectively operated under the same conditions, equipment and catalyst as conventional methanol synthesis.

A methanol plant producing chemical grade methanol was simulated in Aspen Plus. The studied plants have three different annual capacities: 10 kt/a, 50 kt/a and 250 kt/a. They were compared with the option of buying the CO₂ or capturing it directly from flue gases through a carbon capture unit attached to the methanol plant. The kinetic model considering both CO and CO₂ as sources of carbon for methanol formation was described thoroughly, and the main considerations and parameters were introduced for the simulation. The simulation successfully achieved chemical grade methanol production, with a high overall CO₂ conversion rate and close to stoichiometric raw material utilization.

Heat exchanger network was optimized in Aspen Energy Analyzer which achieved a total of 75% heat duty saving. This was accomplished by completely eliminating heating need as steam generated within the methanol plant could cover this need, and decreasing the cold utility to less than half.

The estimated LCOMeOH ranges between 1130 and 630 €/t which is significantly higher than the current listed market price for fossil methanol at 419 €/t. This high LCOMeOH is mostly due to the high production cost of hydrogen, which corresponds to 72% of LCOMeOH. Economies of scale play a substantial effect in decreasing LCOMeOH, as methanol from the 250 kt/a plant has almost half the production cost of the 10 kt/a plant. When considering the source of CO₂, direct buying compared to CC plant, for the smaller plant direct buying is cheaper, while for the largest plant having an own CC plant results in lower LCOMeOH. The influence of cost parameters was investigated in a series of sensitivity analyses. It was revealed that selling the oxygen by-product from water electrolysis had the most significant effect, reducing the LCOMeOH to 475 €/t. However, this option might not be available due to the location of the methanol plant. Cost of electricity also has a significant influence on the LCOMeOH, and for a 10 €/MWh change the

LCOMeOH changed by 110 €/t. Finally, the estimated LCOMeOH was least sensitive for the change in cost of CO₂. When comparing owning a CC plant with purchasing CO₂ from outside sources, it was revealed that purchasing option is only beneficial for smaller plants.

Fossil-free methanol production from CO₂ and H₂ could become competitive with fossil methanol if cost of hydrogen production, which is dominated by electricity cost, would decrease significantly. For electricity cost at 10 €/MWh production of fossil-free methanol could become cheaper in larger plants than fossil methanol.

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Appendix 1

Detailed stream tables for methanol plants

Table A1: Stream table of methanol plant with 10 kt/a output

	<i>BOTTOM</i>	<i>CO2FEED</i>	<i>CO2RICH</i>	<i>FEED</i>	<i>H2FEED</i>	<i>METHANOL</i>	<i>MIX</i>	<i>PRODUCT</i>
<i>Temperature °C</i>	102.54	18.00	30.28	250.00	50.00	30.00	46.52	250.00
<i>Pressure bar</i>	1.00	2.00	1.00	50.00	50.00	1.00	50.00	49.99
<i>Vapour frac</i>	0.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00
<i>Mole flow kmol/h</i>	39.47	40.56	0.59	944.44	121.67	39.05	944.44	865.63
<i>H₂O</i>	39.47	0.00	0.01	0.41	0.00	0.00	0.41	39.90
<i>CH₃OH</i>	0.00	0.00	0.07	2.25	0.00	39.01	2.25	41.65
<i>H₂</i>	0.00	0.00	0.02	788.53	121.67	0.00	788.53	670.23
<i>CO₂</i>	0.00	40.56	0.49	135.95	0.00	0.03	135.95	96.46
<i>CO</i>	0.00	0.00	0.00	17.29	0.00	0.00	17.29	17.38
<i>Mole frac H₂O</i>	1.0000	0.0000	0.0214	0.0004	0.0000	0.0001	0.0004	0.0461
<i>Mole frac CH₃OH</i>	0.0000	0.0000	0.1138	0.0024	0.0000	0.9990	0.0024	0.0481
<i>Mole frac H₂</i>	0.0000	0.0000	0.0335	0.8349	1.0000	0.0000	0.8349	0.7743
<i>Mole frac CO₂</i>	0.0000	1.0000	0.8297	0.1440	0.0000	0.0009	0.1440	0.1114
<i>Mole frac CO</i>	0.0000	0.0000	0.0016	0.0183	0.0000	0.0000	0.0183	0.0201
<i>Mass flow kg/h</i>	711.13	1784.85	24.01	8136.77	245.27	1251.63	8136.77	8136.77
<i>H₂O</i>	711.13	0.00	0.23	7.44	0.00	0.06	7.44	718.90
<i>CH₃OH</i>	0.00	0.00	2.15	72.09	0.00	1250.04	72.09	1334.68
<i>H₂</i>	0.00	0.00	0.04	1589.58	245.27	0.00	1589.58	1351.10
<i>CO₂</i>	0.00	1784.85	21.57	5983.31	0.00	1.53	5983.31	4245.28
<i>CO</i>	0.00	0.00	0.03	484.34	0.00	0.00	484.34	486.81
<i>Mass frac H₂O</i>	1.0000	0.0000	0.0095	0.0009	0.0000	0.0000	0.0009	0.0884
<i>Mass frac CH₃OH</i>	0.0000	0.0000	0.0897	0.0089	0.0000	0.9987	0.0089	0.1640
<i>Mass frac H₂</i>	0.0000	0.0000	0.0017	0.1954	1.0000	0.0000	0.1954	0.1660
<i>Mass frac CO₂</i>	0.0000	1.0000	0.8981	0.7353	0.0000	0.0012	0.7353	0.5217
<i>Mass frac CO</i>	0.0000	0.0000	0.0011	0.0595	0.0000	0.0000	0.0595	0.0598
	<i>PURGE</i>	<i>RAWMEOH</i>	<i>RECYCLE</i>	<i>S1</i>	<i>S2</i>	<i>S3</i>	<i>S4</i>	<i>S5</i>
<i>Temperature °C</i>	29.73	29.73	29.73	93.01	38.00	119.66	38.00	118.20
<i>Pressure bar</i>	45.00	45.00	45.00	4.40	4.40	10.00	10.00	22.30
<i>Vapour frac</i>	1.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00
<i>Mole flow kmol/h</i>	3.93	79.49	786.14	40.56	40.56	40.56	40.56	40.56
<i>H₂O</i>	0.00	39.49	0.42	0.00	0.00	0.00	0.00	0.00
<i>CH₃OH</i>	0.01	39.39	2.26	0.00	0.00	0.00	0.00	0.00
<i>H₂</i>	3.35	0.02	670.21	0.00	0.00	0.00	0.00	0.00
<i>CO₂</i>	0.48	0.58	95.88	40.56	40.56	40.56	40.56	40.56
<i>CO</i>	0.09	0.00	17.38	0.00	0.00	0.00	0.00	0.00
<i>Mole frac H₂O</i>	0.0005	0.4968	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mole frac CH₃OH</i>	0.0029	0.4956	0.0029	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mole frac H₂</i>	0.8525	0.0002	0.8525	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mole frac CO₂</i>	0.1220	0.0073	0.1220	1.0000	1.0000	1.0000	1.0000	1.0000
<i>Mole frac CO</i>	0.0221	0.0000	0.0221	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mass flow kg/h</i>	30.69	1999.42	6137.35	1784.85	1784.85	1784.85	1784.85	1784.85
<i>H₂O</i>	0.04	711.42	7.48	0.00	0.00	0.00	0.00	0.00
<i>CH₃OH</i>	0.36	1262.23	72.46	0.00	0.00	0.00	0.00	0.00
<i>H₂</i>	6.76	0.04	1351.06	0.00	0.00	0.00	0.00	0.00
<i>CO₂</i>	21.10	25.71	4219.57	1784.85	1784.85	1784.85	1784.85	1784.85
<i>CO</i>	2.43	0.03	486.78	0.00	0.00	0.00	0.00	0.00
<i>Mass frac H₂O</i>	0.0012	0.3558	0.0012	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mass frac CH₃OH</i>	0.0118	0.6313	0.0118	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mass frac H₂</i>	0.2201	0.0000	0.2201	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mass frac CO₂</i>	0.6875	0.0129	0.6875	1.0000	1.0000	1.0000	1.0000	1.0000
<i>Mass frac CO</i>	0.0793	0.0000	0.0793	0.0000	0.0000	0.0000	0.0000	0.0000
	<i>S6</i>	<i>S7</i>	<i>S8</i>	<i>S9</i>	<i>S10</i>	<i>S11</i>	<i>S12</i>	<i>S13</i>
<i>Temperature °C</i>	38.00	119.56	30.00	29.73	42.21	30.28	86.80	66.31
<i>Pressure bar</i>	22.30	50.00	49.99	45.00	50.00	1.00	1.00	1.00
<i>Vapour frac</i>	1.00	1.00	0.91	1.00	1.00	0.00	1.00	1.00
<i>Mole flow kmol/h</i>	40.56	40.56	865.63	782.21	782.21	78.90	78.90	63.55
<i>H₂O</i>	0.00	0.00	39.90	0.41	0.41	39.48	39.48	2.60
<i>CH₃OH</i>	0.00	0.00	41.65	2.25	2.25	39.33	39.33	60.85
<i>H₂</i>	0.00	0.00	670.23	666.86	666.86	0.00	0.00	0.00
<i>CO₂</i>	40.56	40.56	96.46	95.40	95.40	0.09	0.09	0.09
<i>CO</i>	0.00	0.00	17.38	17.29	17.29	0.00	0.00	0.00
<i>Mole frac H₂O</i>	0.0000	0.0000	0.0461	0.0005	0.0005	0.5004	0.5004	0.0409
<i>Mole frac CH₃OH</i>	0.0000	0.0000	0.0481	0.0029	0.0029	0.4984	0.4984	0.9576

<i>Mole frac H₂</i>	0.0000	0.0000	0.7743	0.8525	0.8525	0.0000	0.0000	0.0000
<i>Mole frac CO₂</i>	1.0000	1.0000	0.1114	0.1220	0.1220	0.0012	0.0012	0.0015
<i>Mole frac CO</i>	0.0000	0.0000	0.0201	0.0221	0.0221	0.0000	0.0000	0.0000
<i>Mass flow kg/h</i>	1784.85	1784.85	8136.77	6106.66	6106.66	1975.41	1975.41	2000.83
<i>H₂O</i>	0.00	0.00	718.90	7.44	7.44	711.19	711.19	46.84
<i>CH₃OH</i>	0.00	0.00	1334.68	72.09	72.09	1260.07	1260.07	1949.85
<i>H₂</i>	0.00	0.00	1351.10	1344.31	1344.31	0.00	0.00	0.00
<i>CO₂</i>	1784.85	1784.85	4245.28	4198.48	4198.47	4.14	4.14	4.14
<i>CO</i>	0.00	0.00	486.81	484.35	484.34	0.00	0.00	0.00
<i>Mass frac H₂O</i>	0.0000	0.0000	0.0884	0.0012	0.0012	0.3600	0.3600	0.0234
<i>Mass frac CH₃OH</i>	0.0000	0.0000	0.1640	0.0118	0.0118	0.6379	0.6379	0.9745
<i>Mass frac H₂</i>	0.0000	0.0000	0.1660	0.2201	0.2201	0.0000	0.0000	0.0000
<i>Mass frac CO₂</i>	1.0000	1.0000	0.5217	0.6875	0.6875	0.0021	0.0021	0.0021
<i>Mass frac CO</i>	0.0000	0.0000	0.0598	0.0793	0.0793	0.0000	0.0000	0.0000
	S14	S15	S16	VAPOUR	AIR	STEAM	S17	
<i>Temperature °C</i>	66.23	60.25	32.06	60.25	15.00	1495.42	120.00	
<i>Pressure bar</i>	1.00	1.00	1.00	1.00	1.00	1.00	1.00	
<i>Vapour frac</i>	0.00	0.00	1.00	1.00	1.00	1.00	1.00	
<i>Mole flow kmol/h</i>	24.12	39.05	4.89	0.37	17.47	20.83	20.83	
<i>H₂O</i>	2.60	0.00	0.01	0.00	-	-	-	
<i>CH₃OH</i>	21.53	39.01	0.39	0.31	-	-	-	
<i>H₂</i>	0.00	0.00	3.37	0.00	-	-	-	
<i>CO₂</i>	0.00	0.03	1.03	0.06	-	-	-	
<i>CO</i>	0.00	0.00	0.09	0.00	-	-	-	
<i>Mole frac H₂O</i>	0.1076	0.0001	0.0030	0.0000	-	-	-	
<i>Mole frac CH₃OH</i>	0.8924	0.9990	0.0800	0.8409	-	-	-	
<i>Mole frac H₂</i>	0.0000	0.0000	0.6888	0.0000	-	-	-	
<i>Mole frac CO₂</i>	0.0000	0.0009	0.2102	0.1590	-	-	-	
<i>Mole frac CO</i>	0.0000	0.0000	0.0179	0.0000	-	-	-	
<i>Mass flow kg/h</i>	736.55	1251.63	67.34	12.64	504.00	571.34	571.34	
<i>H₂O</i>	46.77	0.06	0.27	0.00	-	-	-	
<i>CH₃OH</i>	689.78	1250.04	12.55	10.04	-	-	-	
<i>H₂</i>	0.00	0.00	6.80	0.00	-	-	-	
<i>CO₂</i>	0.00	1.53	45.27	2.61	-	-	-	
<i>CO</i>	0.00	0.00	2.46	0.00	-	-	-	
<i>Mass frac H₂O</i>	0.0635	0.0000	0.0039	0.0000	-	-	-	
<i>Mass frac CH₃OH</i>	0.9365	0.9987	0.1864	0.7938	-	-	-	
<i>Mass frac H₂</i>	0.0000	0.0000	0.1009	0.0000	-	-	-	
<i>Mass frac CO₂</i>	0.0000	0.0012	0.6722	0.2062	-	-	-	
<i>Mass frac CO</i>	0.0000	0.0000	0.0365	0.0000	-	-	-	

Table A2: Stream table of methanol plant with 50 kt/a output

	<i>BOTTOM</i>	<i>CO2FEED</i>	<i>CO2RICH</i>	<i>FEED</i>	<i>H2FEED</i>	<i>METHANOL</i>	<i>MIX</i>	<i>PRODUCT</i>
<i>Temperature °C</i>	102.54	18.00	30.28	250.00	50.00	30.00	46.51	250.00
<i>Pressure bar</i>	1.00	2.00	1.00	50.00	50.00	1.00	50.00	49.99
<i>Vapour frac</i>	0.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00
<i>Mole flow kmol/h</i>	197.48	202.88	2.95	4724.65	608.64	195.22	4724.65	4330.42
<i>H₂O</i>	197.48	0.00	0.06	2.07	0.00	0.00	2.07	199.62
<i>CH₃OH</i>	0.00	0.00	0.34	11.26	0.00	195.06	11.26	208.37
<i>H₂</i>	0.00	0.00	0.10	3944.68	608.64	0.00	3944.68	3352.89
<i>CO₂</i>	0.00	202.88	2.45	680.15	0.00	0.17	680.15	482.59
<i>CO</i>	0.00	0.00	0.00	86.50	0.00	0.00	86.50	86.94
<i>Mole frac H₂O</i>	1.0000	0.0000	0.0214	0.0004	0.0000	0.0000	0.0004	0.0461
<i>Mole frac CH₃OH</i>	0.0000	0.0000	0.1138	0.0024	0.0000	0.9991	0.0024	0.0481
<i>Mole frac H₂</i>	0.0000	0.0000	0.0335	0.8349	1.0000	0.0000	0.8349	0.7743
<i>Mole frac CO₂</i>	0.0000	1.0000	0.8297	0.1440	0.0000	0.0009	0.1440	0.1114
<i>Mole frac CO</i>	0.0000	0.0000	0.0016	0.0183	0.0000	0.0000	0.0183	0.0201
<i>Mass flow kg/h</i>	3557.72	8928.73	120.14	40705.93	1226.95	6257.41	40705.93	40705.93
<i>H₂O</i>	3557.72	0.00	1.14	37.22	0.00	0.00	37.22	3596.27
<i>CH₃OH</i>	0.00	0.00	10.77	360.66	0.00	6250.01	360.66	6676.73
<i>H₂</i>	0.00	0.00	0.20	7952.00	1226.95	0.00	7952.00	6759.02
<i>CO₂</i>	0.00	8928.73	107.89	29933.10	0.00	7.40	29933.10	21238.64
<i>CO</i>	0.00	0.00	0.13	2422.95	0.00	0.00	2422.95	2435.26
<i>Mass frac H₂O</i>	1.0000	0.0000	0.0095	0.0009	0.0000	0.0000	0.0009	0.0883
<i>Mass frac CH₃OH</i>	0.0000	0.0000	0.0897	0.0089	0.0000	0.9988	0.0089	0.1640
<i>Mass frac H₂</i>	0.0000	0.0000	0.0017	0.1954	1.0000	0.0000	0.1954	0.1660
<i>Mass frac CO₂</i>	0.0000	1.0000	0.8981	0.7353	0.0000	0.0012	0.7353	0.5218
<i>Mass frac CO</i>	0.0000	0.0000	0.0011	0.0595	0.0000	0.0000	0.0595	0.0598
	PURGE	RAWMEOH	RECYCLE	S1	S2	S3	S4	S5
<i>Temperature °C</i>	29.73	29.73	29.73	93.01	38.00	119.66	38.00	118.20

<i>Pressure bar</i>	45.00	45.00	45.00	4.40	4.40	10.00	10.00	22.30
<i>Vapour frac</i>	1.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00
<i>Mole flow kmol/h</i>	19.66	397.63	3932.78	202.88	202.88	202.88	202.88	202.88
<i>H₂O</i>	0.01	197.55	2.08	0.00	0.00	0.00	0.00	0.00
<i>CH₃OH</i>	0.06	197.06	11.31	0.00	0.00	0.00	0.00	0.00
<i>H₂</i>	16.76	0.10	3352.79	0.00	0.00	0.00	0.00	0.00
<i>CO₂</i>	2.40	2.92	479.67	202.88	202.88	202.88	202.88	202.88
<i>CO</i>	0.43	0.00	86.94	0.00	0.00	0.00	0.00	0.00
<i>Mole frac H₂O</i>	0.0005	0.4968	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mole frac CH₃OH</i>	0.0029	0.4956	0.0029	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mole frac H₂</i>	0.8525	0.0002	0.8525	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mole frac CO₂</i>	0.1220	0.0073	0.1220	1.0000	1.0000	1.0000	1.0000	1.0000
<i>Mole frac CO</i>	0.0221	0.0000	0.0221	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mass flow kg/h</i>	153.52	10002.07	30703.86	8928.73	8928.73	8928.73	8928.73	8928.73
<i>H₂O</i>	0.19	3558.86	37.41	0.00	0.00	0.00	0.00	0.00
<i>CH₃OH</i>	1.81	6314.27	362.47	0.00	0.00	0.00	0.00	0.00
<i>H₂</i>	33.79	0.20	6758.82	0.00	0.00	0.00	0.00	0.00
<i>CO₂</i>	105.55	128.61	21110.03	8928.73	8928.73	8928.73	8928.73	8928.73
<i>CO</i>	12.18	0.13	2435.13	0.00	0.00	0.00	0.00	0.00
<i>Mass frac H₂O</i>	0.0012	0.3558	0.0012	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mass frac CH₃OH</i>	0.0118	0.6313	0.0118	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mass frac H₂</i>	0.2201	0.0000	0.2201	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Mass frac CO₂</i>	0.6875	0.0129	0.6875	1.0000	1.0000	1.0000	1.0000	1.0000
<i>Mass frac CO</i>	0.0793	0.0000	0.0793	0.0000	0.0000	0.0000	0.0000	0.0000
<i>Temperature °C</i>	S6	S7	S8	S9	S10	S11	S12	S13
<i>Pressure bar</i>	118.20	38.00	119.56	30.00	42.21	30.28	86.80	66.37
<i>Vapour frac</i>	22.30	22.30	50.00	49.99	50.00	1.00	1.00	1.00
<i>Mole flow kmol/h</i>	1.00	1.00	1.00	0.91	1.00	0.00	1.00	1.00
<i>H₂O</i>	202.88	202.88	202.88	4330.42	3913.13	394.68	394.68	317.75
<i>CH₃OH</i>	0.00	0.00	199.62	2.07	2.07	197.48	197.48	13.43
<i>H₂</i>	0.00	0.00	208.37	11.26	11.26	196.73	196.73	303.84
<i>CO₂</i>	0.00	0.00	3352.89	3336.03	3336.04	0.00	0.00	0.00
<i>CO</i>	202.88	202.88	482.59	477.27	477.27	0.47	0.47	0.47
<i>Mole frac H₂O</i>	0.0000	0.0000	0.0461	0.0005	0.0005	0.5004	0.5004	0.0423
<i>Mole frac CH₃OH</i>	0.0000	0.0000	0.0481	0.0029	0.0029	0.4984	0.4984	0.9562
<i>Mole frac H₂</i>	0.0000	0.0000	0.7743	0.8525	0.8525	0.0000	0.0000	0.0000
<i>Mole frac CO₂</i>	1.0000	1.0000	0.1114	0.1220	0.1220	0.0012	0.0012	0.0015
<i>Mole frac CO</i>	0.0000	0.0000	0.0201	0.0221	0.0221	0.0000	0.0000	0.0000
<i>Mass flow kg/h</i>	8928.73	8928.73	8928.73	40705.93	30550.26	9881.93	9881.93	9998.52
<i>H₂O</i>	0.00	0.00	3596.27	37.22	37.22	3557.72	3557.72	241.99
<i>CH₃OH</i>	0.00	0.00	6676.73	360.66	360.66	6303.50	6303.50	9735.82
<i>H₂</i>	0.00	0.00	6759.02	6725.03	6725.06	0.00	0.00	0.00
<i>CO₂</i>	8928.73	8928.73	21238.64	21004.48	21004.37	20.72	20.72	20.72
<i>CO</i>	0.00	0.00	2435.26	2422.96	2422.95	0.00	0.00	0.00
<i>Mass frac H₂O</i>	0.0000	0.0000	0.0000	0.0883	0.0012	0.0012	0.3600	0.3600
<i>Mass frac CH₃OH</i>	0.0000	0.0000	0.0000	0.1640	0.0118	0.0118	0.6379	0.6379
<i>Mass frac H₂</i>	0.0000	0.0000	0.0000	0.1660	0.2201	0.2201	0.0000	0.0000
<i>Mass frac CO₂</i>	1.0000	1.0000	1.0000	0.5218	0.6875	0.6875	0.0021	0.0021
<i>Mass frac CO</i>	0.0000	0.0000	0.0000	0.0598	0.0793	0.0793	0.0000	0.0000
<i>Temperature °C</i>	S14	S15	S16	VAPOUR	AIR	STEAM	S17	
<i>Pressure bar</i>	66.29	60.41	32.25	60.41	15.00	1509.32	120.00	
<i>Vapour frac</i>	1.00	1.00	1.00	1.00	1.00	1.00	1.00	
<i>Mole flow kmol/h</i>	0.00	0.00	1.00	1.00	1.00	1.00	1.00	
<i>H₂O</i>	120.55	195.22	24.59	1.97	87.35	104.32	104.32	
<i>CH₃OH</i>	13.43	0.00	0.07	0.00	-	-	-	
<i>H₂</i>	107.12	195.06	2.06	1.67	-	-	-	
<i>CO₂</i>	0.00	0.00	16.86	0.00	-	-	-	
<i>CO</i>	0.00	0.17	5.15	0.30	-	-	-	
<i>Mole frac H₂O</i>	0.00	0.00	0.44	0.00	-	-	-	
<i>Mole frac CH₃OH</i>	0.1114	0.0000	0.0030	0.0000	-	-	-	
<i>Mole frac H₂</i>	0.8886	0.9991	0.0839	0.8465	-	-	-	
<i>Mole frac CO₂</i>	0.0000	0.0000	0.6858	0.0000	-	-	-	
<i>Mole frac CO</i>	0.0000	0.0009	0.2095	0.1535	-	-	-	
<i>Mass flow kg/h</i>	0.0000	0.0000	0.0179	0.0000	-	-	-	
<i>H₂O</i>	3674.31	6257.41	340.46	66.81	2520.0	2860.46	2860.46	
<i>CH₃OH</i>	241.99	0.00	1.33	0.00	-	-	-	
<i>H₂</i>	3432.32	6250.01	66.07	53.49	-	-	-	
<i>CO₂</i>	0.00	0.00	33.99	0.00	-	-	-	
<i>CO</i>	0.00	7.40	226.76	13.32	-	-	-	
<i>Mass frac H₂O</i>	0.00	0.00	12.31	0.00	-	-	-	
<i>Mass frac CH₃OH</i>	0.0659	0.0000	0.0039	0.0000	-	-	-	
<i>Mass frac H₂</i>	0.9341	0.9988	0.1941	0.8006	-	-	-	

Mass frac H ₂	0.0000	0.0000	0.0998	0.0000	-	-	-
Mass frac CO ₂	0.0000	0.0012	0.6660	0.1994	-	-	-
Mass frac CO	0.0000	0.0000	0.0362	0.0000	-	-	-

Table A3: Stream table of methanol plant with 250 kt/a output

	BOTTOM	CO2FEED	CO2RICH	FEED	H2FEED	METHANOL	MIX	PRODUCT
Temperature °C	102.54	18.00	30.28	250.00	50.00	30.00	46.52	250.00
Pressure bar	1.00	2.00	1.00	50.00	50.00	1.00	50.00	49.99
Vapour frac	0.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00
Mole flow kmol/h	986.81	1013.89	14.79	23600.12	3041.66	976.23	23600.12	21629.97
H ₂ O	986.81	0.00	0.32	10.32	0.00	0.08	10.32	997.59
CH ₃ OH	0.00	0.00	1.68	56.23	0.00	975.28	56.23	1041.30
H ₂	0.00	0.00	0.49	19699.70	3041.66	0.00	19699.70	16742.29
CO ₂	0.00	1013.89	12.27	3401.34	0.00	0.87	3401.34	2414.07
CO	0.00	0.00	0.02	432.53	0.00	0.00	432.53	434.73
Mole frac H ₂ O	1.0000	0.0000	0.0214	0.0004	0.0000	0.0001	0.0004	0.0461
Mole frac CH ₃ OH	0.0000	0.0000	0.1138	0.0024	0.0000	0.9990	0.0024	0.0481
Mole frac H ₂	0.0000	0.0000	0.0335	0.8347	1.0000	0.0000	0.8347	0.7740
Mole frac CO ₂	0.0000	1.0000	0.8298	0.1441	0.0000	0.0009	0.1441	0.1116
Mole frac CO	0.0000	0.0000	0.0016	0.0183	0.0000	0.0000	0.0183	0.0201
Mass flow kg/h	17777.73	44621.00	601.44	203507.0	6131.63	31289.84	203507.0	203507.00
H ₂ O	17777.73	0.00	5.71	185.94	0.00	1.52	185.94	17971.84
CH ₃ OH	0.00	0.00	53.92	1801.57	0.00	31249.95	1801.57	33365.40
H ₂	0.00	0.00	1.00	39712.23	6131.63	0.00	39712.23	33750.45
CO ₂	0.00	44621.00	540.15	149692.0	0.00	38.37	149692.0	106243.00
CO	0.00	0.00	0.67	12115.40	0.00	0.00	12115.40	12176.90
Mass frac H ₂ O	1.0000	0.0000	0.0095	0.0009	0.0000	0.0000	0.0009	0.0883
Mass frac CH ₃ OH	0.0000	0.0000	0.0896	0.0089	0.0000	0.9987	0.0089	0.1640
Mass frac H ₂	0.0000	0.0000	0.0017	0.1951	1.0000	0.0000	0.1951	0.1658
Mass frac CO ₂	0.0000	1.0000	0.8981	0.7356	0.0000	0.0012	0.7356	0.5221
Mass frac CO	0.0000	0.0000	0.0011	0.0595	0.0000	0.0000	0.0595	0.0598
Temperature °C	PURGE	RAWMEOH	RECYCLE	S1	S2	S3	S4	S5
Pressure bar	29.73	29.73	29.73	93.01	38.00	119.66	38.00	118.20
Vapour frac	45.00	45.00	45.00	4.40	4.40	10.00	10.00	22.30
Mole flow kmol/h	1.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00
H ₂ O	98.21	1987.15	19642.82	1013.89	1013.89	1013.89	1013.89	1013.89
CH ₃ OH	0.05	987.22	10.37	0.00	0.00	0.00	0.00	0.00
H ₂	0.28	984.79	56.51	0.00	0.00	0.00	0.00	0.00
CO ₂	83.71	0.50	16741.79	0.00	0.00	0.00	0.00	0.00
CO	12.00	14.63	2399.44	1013.89	1013.89	1013.89	1013.89	1013.89
Mole frac H ₂ O	2.17	0.02	434.70	0.00	0.00	0.00	0.00	0.00
Mole frac CH ₃ OH	0.0005	0.4968	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000
Mole frac H ₂	0.0029	0.4956	0.0029	0.0000	0.0000	0.0000	0.0000	0.0000
Mole frac CO ₂	0.8523	0.0002	0.8523	0.0000	0.0000	0.0000	0.0000	0.0000
Mole frac CO	0.1222	0.0074	0.1222	1.0000	1.0000	1.0000	1.0000	1.0000
Mass flow kg/h	0.0221	0.0000	0.0221	0.0000	0.0000	0.0000	0.0000	0.0000
H ₂ O	767.61	49985.08	153522.00	44621.00	44621.00	44621.00	44621.00	44621.00
CH ₃ OH	0.93	17784.96	186.87	0.00	0.00	0.00	0.00	0.00
H ₂	9.05	31554.77	1810.63	0.00	0.00	0.00	0.00	0.00
CO ₂	168.75	1.00	33749.45	0.00	0.00	0.00	0.00	0.00
CO	528.00	643.68	105599.00	44621.00	44621.00	44621.00	44621.00	44621.00
Mass frac H ₂ O	60.88	0.67	12176.24	0.00	0.00	0.00	0.00	0.00
Mass frac CH ₃ OH	0.0012	0.3558	0.0012	0.0000	0.0000	0.0000	0.0000	0.0000
Mass frac H ₂	0.0118	0.6313	0.0118	0.0000	0.0000	0.0000	0.0000	0.0000
Mass frac CO ₂	0.2198	0.0000	0.2198	0.0000	0.0000	0.0000	0.0000	0.0000
Mass frac CO	0.6878	0.0129	0.6878	1.0000	1.0000	1.0000	1.0000	1.0000
Temperature °C	0.0793	0.0000	0.0793	0.0000	0.0000	0.0000	0.0000	0.0000
Pressure bar	S6	S7	S8	S9	S10	S11	S12	S13
Vapour frac	38.00	119.56	30.00	29.73	42.21	30.28	86.80	66.31
Mole flow kmol/h	22.30	50.00	49.99	45.00	50.00	1.00	1.00	1.00
H ₂ O	1.00	1.00	0.91	1.00	1.00	0.00	1.00	1.00
CH ₃ OH	1013.89	1013.89	21629.97	19544.61	19544.57	1972.36	1972.36	1588.62
H ₂	0.00	0.00	997.59	10.32	10.32	986.90	986.90	64.99
CO ₂	0.00	0.00	1041.30	56.23	56.23	983.11	983.11	1521.28
CO	0.00	0.00	16742.29	16658.09	16658.04	0.00	0.00	0.00
Mole frac H ₂ O	1013.89	1013.89	2414.07	2387.45	2387.45	2.35	2.35	2.35
Mole frac CH ₃ OH	0.00	0.00	434.73	432.53	432.53	0.00	0.00	0.00
Mole frac H ₂	0.0000	0.0000	0.0461	0.0005	0.0005	0.5004	0.5004	0.0409
Mole frac CO ₂	0.0000	0.0000	0.0481	0.0029	0.0029	0.4984	0.4984	0.9576
Mole frac CO	0.0000	0.0000	0.7740	0.8523	0.8523	0.0000	0.0000	0.0000

<i>Mole frac CO₂</i>	1.0000	1.0000	0.1116	0.1222	0.1222	0.0012	0.0012	0.0015
<i>Mole frac CO</i>	0.0000	0.0000	0.0201	0.0221	0.0221	0.0000	0.0000	0.0000
<i>Mass flow kg/h</i>	44621.00	44621.00	203507.00	152755.0	152755.0	49383.65	49383.65	50019.33
<i>H₂O</i>	0.00	0.00	17971.84	185.94	185.94	17779.25	17779.25	1170.77
<i>CH₃OH</i>	0.00	0.00	33365.40	1801.57	1801.57	31500.86	31500.86	48745.02
<i>H₂</i>	0.00	0.00	33750.45	33580.70	33580.60	0.00	0.00	0.00
<i>CO₂</i>	44621.00	44621.00	106243.00	105071.0	105071.0	103.53	103.53	103.53
<i>CO</i>	0.00	0.00	12176.90	12115.35	12115.40	0.00	0.00	0.00
<i>Mass frac H₂O</i>	0.0000	0.0000	0.0883	0.0012	0.0012	0.3600	0.3600	0.0234
<i>Mass frac CH₃OH</i>	0.0000	0.0000	0.1640	0.0118	0.0118	0.6379	0.6379	0.9745
<i>Mass frac H₂</i>	0.0000	0.0000	0.1658	0.2198	0.2198	0.0000	0.0000	0.0000
<i>Mass frac CO₂</i>	1.0000	1.0000	0.5221	0.6878	0.6878	0.0021	0.0021	0.0021
<i>Mass frac CO</i>	0.0000	0.0000	0.0598	0.0793	0.0793	0.0000	0.0000	0.0000
	S14	S15	S16	VAPOUR	AIR	STEAM	S17	
<i>Temperature °C</i>	66.23	60.25	32.06	60.25	15.00	1494.70	120.00	
<i>Pressure bar</i>	1.00	1.00	1.00	1.00	1.00	1.00	1.00	
<i>Vapour frac</i>	0.00	0.00	1.00	1.00	1.00	1.00	1.00	
<i>Mole flow kmol/h</i>	603.07	976.23	122.32	9.31	436.74	520.75	520.75	
<i>H₂O</i>	64.90	0.08	0.37	0.00	-	-	-	
<i>CH₃OH</i>	538.17	975.28	9.80	7.83	-	-	-	
<i>H₂</i>	0.00	0.00	84.20	0.00	-	-	-	
<i>CO₂</i>	0.00	0.87	25.75	1.48	-	-	-	
<i>CO</i>	0.00	0.00	2.20	0.00	-	-	-	
<i>Mole frac H₂O</i>	0.1076	0.0001	0.0030	0.0000	-	-	-	
<i>Mole frac CH₃OH</i>	0.8924	0.9990	0.0801	0.8409	-	-	-	
<i>Mole frac H₂</i>	0.0000	0.0000	0.6884	0.0000	-	-	-	
<i>Mole frac CO₂</i>	0.0000	0.0009	0.2105	0.1590	-	-	-	
<i>Mole frac CO</i>	0.0000	0.0000	0.0180	0.0000	-	-	-	
<i>Mass flow kg/h</i>	18413.41	31289.84	1685.11	316.06	12600.00	14285.11	14285.11	
<i>H₂O</i>	1169.25	1.52	6.65	0.00	-	-	-	
<i>CH₃OH</i>	17244.16	31249.95	313.86	250.89	-	-	-	
<i>H₂</i>	0.00	0.00	169.75	0.00	-	-	-	
<i>CO₂</i>	0.00	38.37	1133.31	65.16	-	-	-	
<i>CO</i>	0.00	0.00	61.55	0.00	-	-	-	
<i>Mass frac H₂O</i>	0.0635	0.0000	0.0039	0.0000	-	-	-	
<i>Mass frac CH₃OH</i>	0.9365	0.9987	0.1863	0.7938	-	-	-	
<i>Mass frac H₂</i>	0.0000	0.0000	0.1007	0.0000	-	-	-	
<i>Mass frac CO₂</i>	0.0000	0.0012	0.6725	0.2062	-	-	-	
<i>Mass frac CO</i>	0.0000	0.0000	0.0365	0.0000	-	-	-	

Appendix 2

Heat streams for methanol plants with 10 kt/a and 250 kt/a output

Table A4: Heat stream for methanol plant with 10 kt/a output

<i>Stream</i>	<i>Stream type</i>	<i>Supply temperature [°C]</i>	<i>Target temperature [°C]</i>	<i>Duty [kW]</i>	<i>CP [kW/°C]</i>
<i>HX1</i>	Hot	93.01	38.00	24.76	0.45
<i>HX2</i>	Hot	119.66	38.00	38.11	0.47
<i>HX3</i>	Hot	118.20	38.00	39.70	0.50
<i>HX4</i>	Cold	46.52	250.00	1687.87	8.29
<i>HX5</i>	Hot	250.00	30.00	2657.51	68.40
<i>HX6</i>	Cold	30.28	86.80	997.89	141.26
<i>HX7</i>	Hot	60.25	30.00	39.67	1.31
<i>REBOILER at DISTL</i>	Cold	102.54	103.04	282.98	565.97
<i>REBOILER at RECT</i>	Cold	65.71	66.23	206.53	1206.02
<i>CONDENSER at DISTL</i>	Hot	67.81	66.31	519.06	1455.49
<i>CONDENSER at RECT</i>	Hot	64.40	60.25	888.22	6772.72
<i>REACTOR HEAT</i>	Hot	250.00	249.50	655.53	1311.05
<i>HX8</i>	Hot	1495.42	120.00	288.85	0.63

Table A5: Heat streams for methanol plant with 250 kt/a output

<i>Stream</i>	<i>Stream type</i>	<i>Supply temperature [°C]</i>	<i>Target temperature [°C]</i>	<i>Duty [MW]</i>	<i>CP [kW/°C]</i>
<i>HX1</i>	Hot	93.01	38.00	0.62	11.25
<i>HX2</i>	Hot	119.66	38.00	0.95	11.67
<i>HX3</i>	Hot	118.20	38.00	0.99	12.38
<i>HX4</i>	Cold	46.52	250.00	42.18	207.30
<i>HX5</i>	Hot	250.00	30.00	66.42	1709.49
<i>HX6</i>	Cold	30.28	86.80	24.95	3531.31
<i>HX7</i>	Hot	60.25	30.00	0.99	32.78
<i>REBOILER at DISTL</i>	Cold	102.54	103.04	7.07	14148.71
<i>REBOILER at RECT</i>	Cold	65.71	66.23	5.16	30152.00
<i>CONDENSER at DISTL</i>	Hot	67.81	66.31	12.98	36388.67
<i>CONDENSER at RECT</i>	Hot	64.40	60.25	22.20	169296.11
<i>REACTOR HEAT</i>	Hot	250.00	249.50	16.39	32776.04
<i>HX8</i>	Hot	1494.70	120.00	7.22	15.75

Appendix 3

Composite Curves and Grand Composite Curve

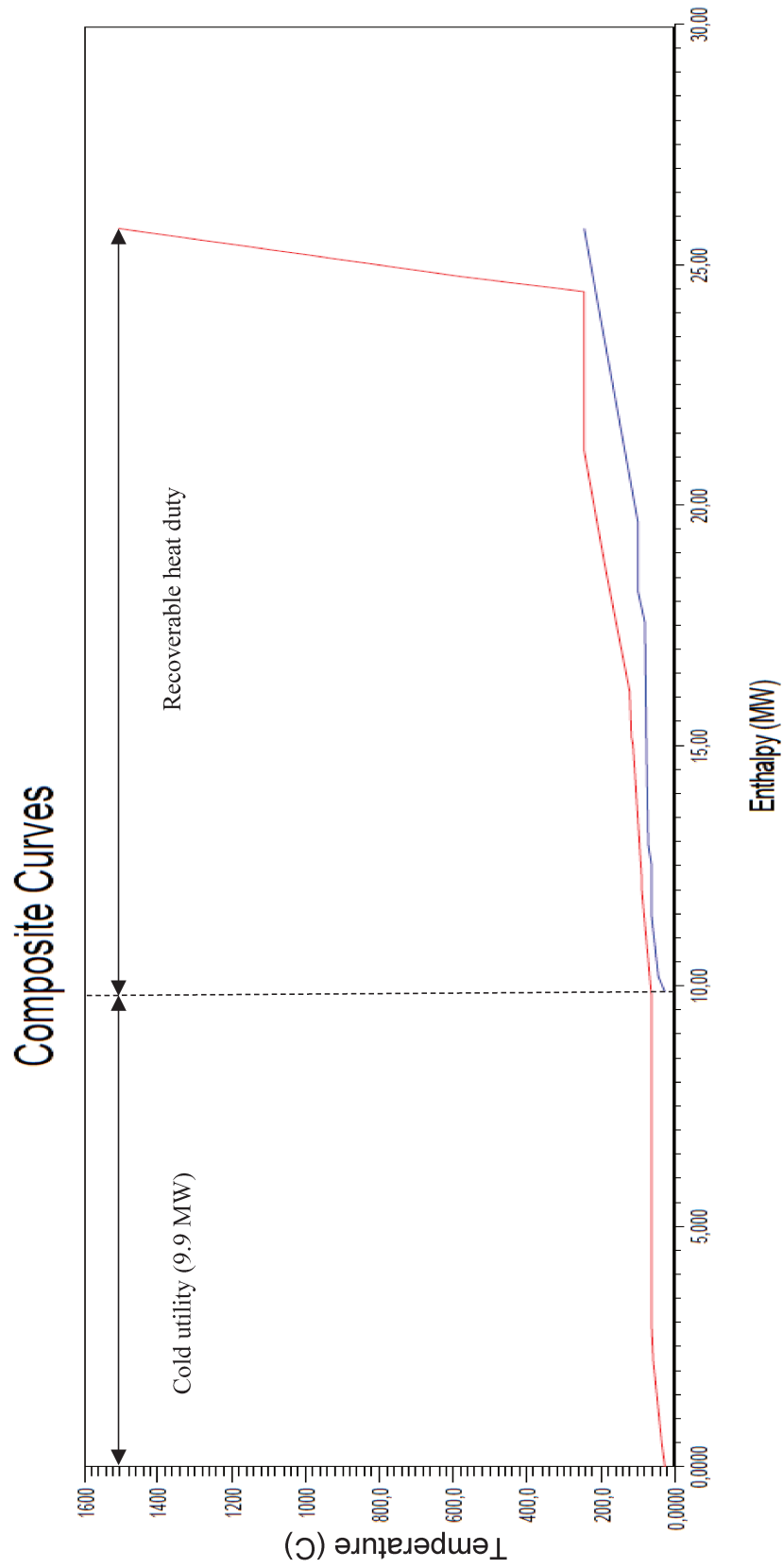


Figure A1: Composite Curves for the 50 kt/a methanol plant (blue curve = cold streams, red curve = hot streams)

Grand Composite Curve

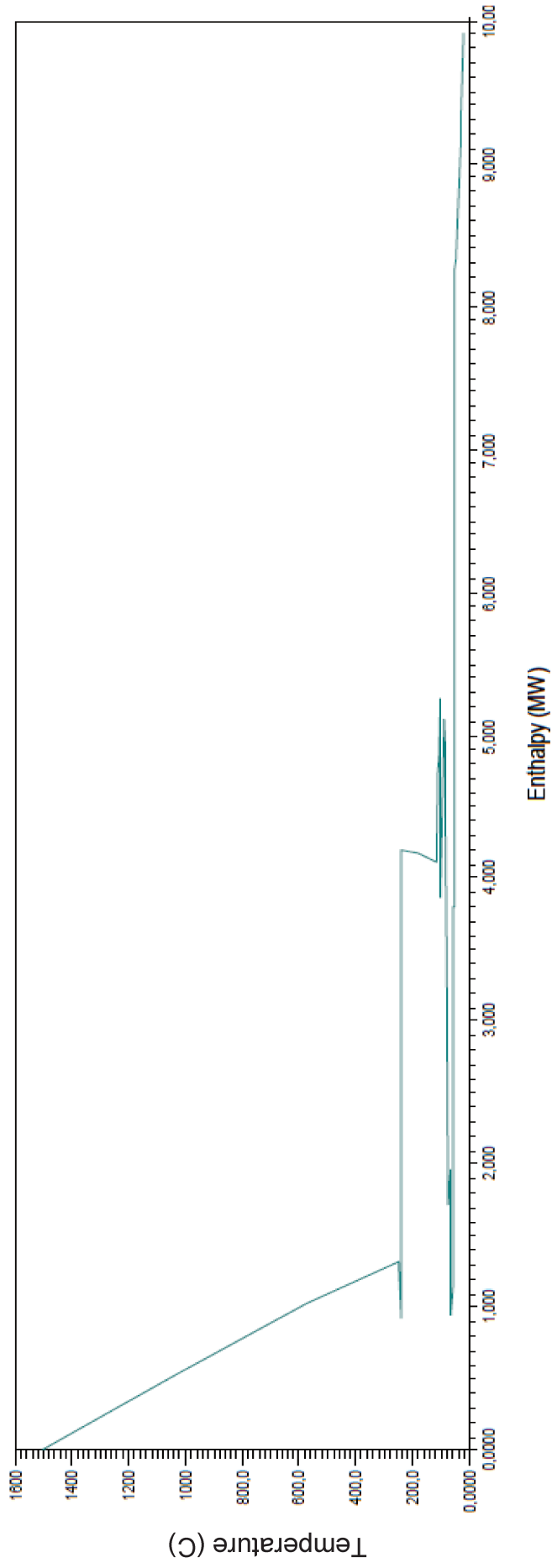


Figure A2: Grand Composite Curve for the 50 kt/a methanol plant

Appendix 4

Heat exchanger network designs

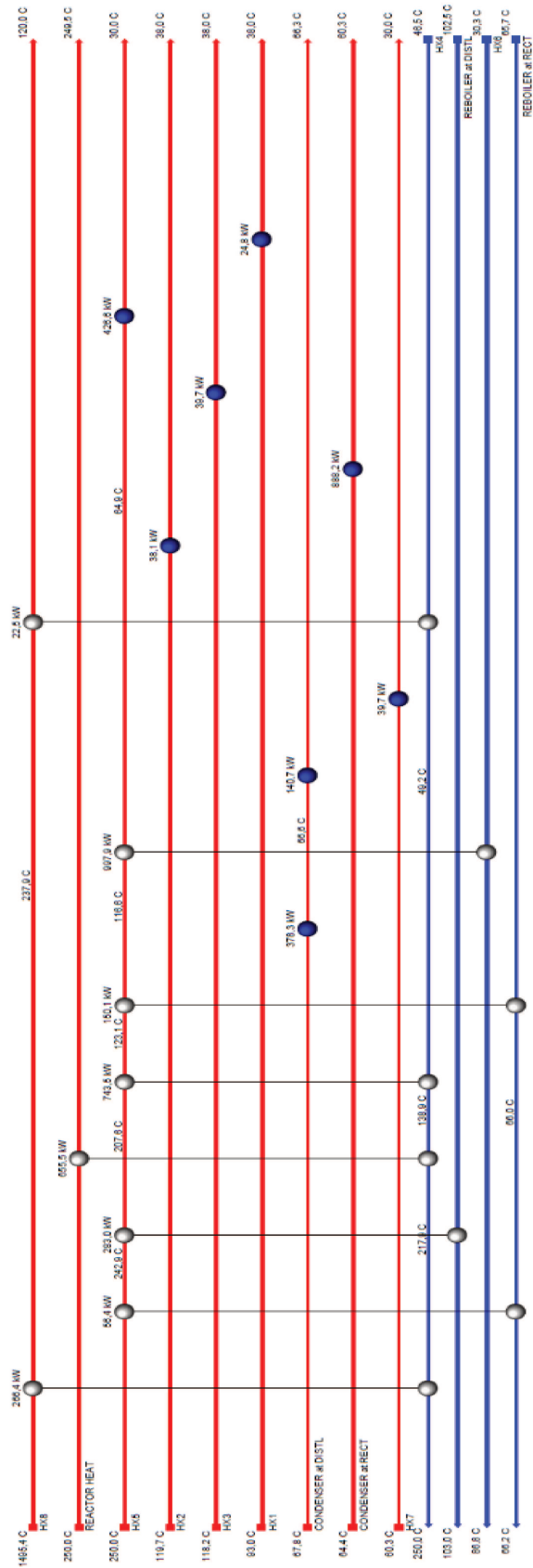


Figure A3: Heat exchanger network design for methanol plant with 10 kt/a output (red line = hot stream, blue line = cold stream, blue dot = cooling water)

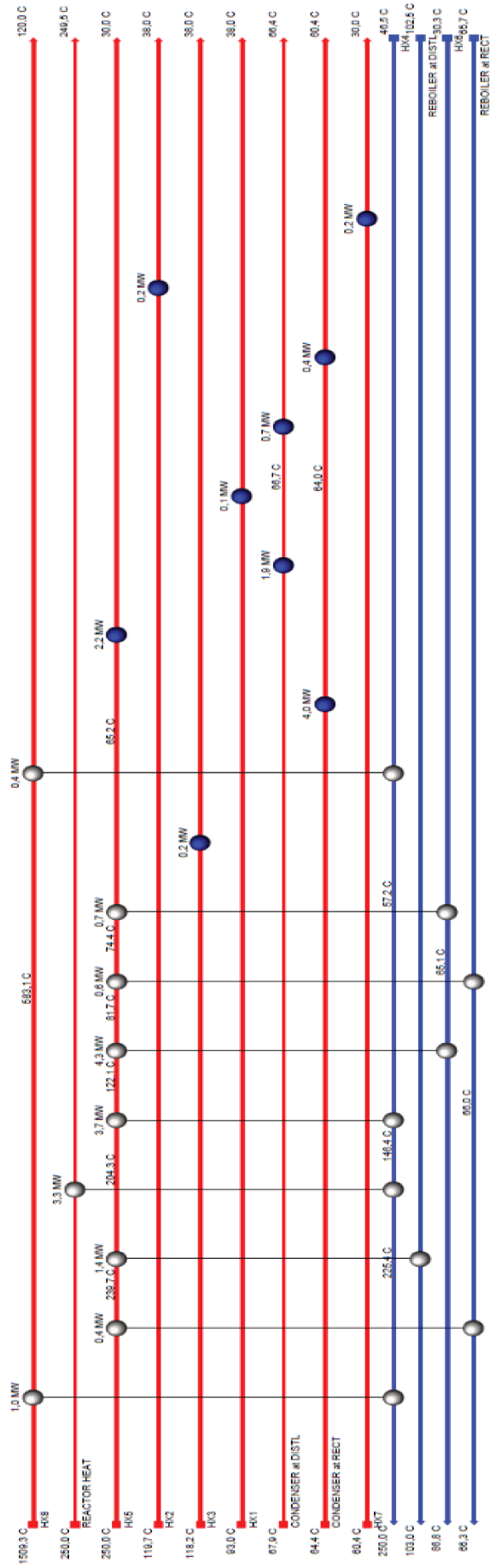


Figure A4: Heat exchanger network design for methanol plant with 50kt/a output (red line = hot stream, blue line = cold stream, blue dot = cooling water)

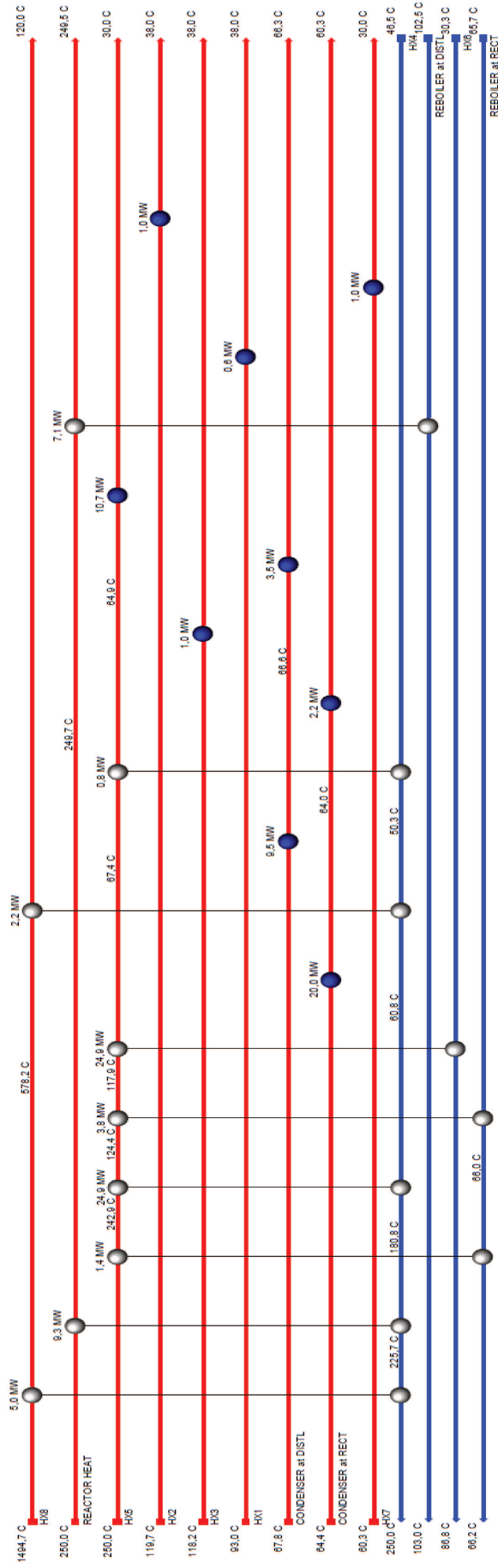


Figure A5: Heat exchanger network design for methanol plant with 250 kt/a output (red line = hot stream, blue line = cold stream, blue dot = cooling water)

Appendix 5

List of heat exchangers from HEN designs after heat integration

Table A6: Heat exchangers for methanol plant with 10 kt/a output after heat integration

<i>HX</i>	<i>Duty [kW]</i>	<i>Area [m²]</i>	<i>Shells</i>	<i>Hot stream</i>	<i>Hot in [°C]</i>	<i>Hot out [°C]</i>	<i>Cold stream</i>	<i>Cold in [°C]</i>	<i>Cold out [°C]</i>
<i>E-104</i>	56.41	0.91	1	HX5	250.00	242.95	REBOILER at RECT	66.05	66.23
<i>E-105</i>	266.35	49.49	3	HX8	1495.42	237.88	HX4	217.89	250.00
<i>E-106</i>	888.22	7.85	1	CONDENSER at RECT	64.40	60.25	Cooling Water	19.80	23.00
<i>E-107</i>	378.35	8.22	1	CONDENSER at DISTL	67.81	66.58	Cooling Water	19.80	23.00
<i>E-108</i>	655.53	86.78	1	REACTOR HEAT	250.00	249.50	HX4	138.86	217.89
<i>E-109</i>	282.98	18.12	1	HX5	242.95	207.58	REBOILER at DISTL	102.54	103.04
<i>E-110</i>	743.50	81.45	2	HX5	207.58	123.07	HX4	49.23	138.86
<i>E-111</i>	140.72	1.47	1	CONDENSER at DISTL	66.58	66.31	Cooling Water	19.44	19.80
<i>E-112</i>	150.12	2.80	1	HX5	123.07	116.58	REBOILER at RECT	65.71	66.05
<i>E-113</i>	997.89	107.56	2	HX5	116.58	64.89	HX6	30.28	86.80
<i>E-114</i>	38.11	11.75	1	HX2	119.66	38.00	Cooling Water	19.08	19.44
<i>E-115</i>	24.76	14.88	1	HX1	93.01	38.00	Cooling Water	19.08	19.44
<i>E-116</i>	39.67	1.33	1	HX7	60.25	30.00	Cooling Water	19.08	19.44
<i>E-117</i>	39.70	7.72	1	HX3	118.20	38.00	Cooling Water	19.08	19.44
<i>E-118</i>	22.49	10.38	1	HX8	237.88	120.00	HX4	46.52	49.23
<i>E-119</i>	426.61	18.22	1	HX5	64.89	30.00	Cooling Water	18.00	19.08

Table A7: Heat exchangers for methanol plant with 50 kt/a output

<i>HX</i>	<i>Duty [kW]</i>	<i>Area [m²]</i>	<i>Shells</i>	<i>Hot stream</i>	<i>Hot in [°C]</i>	<i>Hot out [°C]</i>	<i>Cold stream</i>	<i>Cold in [°C]</i>	<i>Cold out [°C]</i>
<i>E-104</i>	413.42	6.73	1	HX5	250.00	239.67	REBOILER at RECT	66.03	66.29
<i>E-105</i>	1021.01	86.14	1	HX8	1509.32	583.11	HX4	225.40	250.00
<i>E-106</i>	3991.78	33.59	1	CONDENSER at RECT	64.40	64.05	Cooling Water	20.03	23.00
<i>E-107</i>	1889.52	41.34	1	CONDENSER at DISTL	67.92	66.65	Cooling Water	20.03	23.00
<i>E-108</i>	3279.27	503.26	2	REACTOR HEAT	250.00	249.50	HX4	146.37	225.40
<i>E-109</i>	1415.74	93.18	1	HX5	239.67	204.29	REBOILER at DISTL	102.54	103.04
<i>E-110</i>	3700.54	476.01	2	HX5	204.29	122.10	HX4	57.19	146.37
<i>E-111</i>	4255.88	283.47	2	HX5	122.10	81.67	HX6	65.11	86.80
<i>E-112</i>	702.59	7.39	1	CONDENSER at DISTL	66.65	66.37	Cooling Water	19.67	20.03
<i>E-113</i>	619.04	43.14	1	HX5	81.67	74.44	REBOILER at RECT	65.72	66.03
<i>E-114</i>	443.10	110.00	2	HX8	583.11	120.00	HX4	46.51	57.19
<i>E-115</i>	447.83	5.40	1	CONDENSER at RECT	64.05	60.41	Cooling Water	19.45	19.67
<i>E-116</i>	736.04	49.30	2	HX5	74.44	65.21	HX6	30.28	65.11
<i>E-117</i>	190.64	58.77	1	HX2	119.66	38.00	Cooling Water	19.09	19.45
<i>E-118</i>	123.85	74.45	1	HX1	93.01	38.00	Cooling Water	19.09	19.45
<i>E-119</i>	199.33	6.69	1	HX7	60.41	30.00	Cooling Water	19.09	19.45
<i>E-120</i>	198.61	38.64	1	HX3	118.20	38.00	Cooling Water	19.09	19.45
<i>E-121</i>	2153.74	91.63	1	HX5	65.21	30.00	Cooling Water	18.00	19.09

Table A8: Heat exchangers for methanol plant with 250 kt/a output

<i>HX</i>	<i>Duty</i> [MW]	<i>Area</i> [m ²]	<i>Shells</i>	<i>Hot stream</i>	<i>Hot in</i> [°C]	<i>Hot out</i> [°C]	<i>Cold stream</i>	<i>Cold in</i> [°C]	<i>Cold out</i> [°C]
<i>E-104</i>	1.41	22.80	1	HX5	250.00	242.95	REBOILER at RECT	66.05	66.23
<i>E-105</i>	5.03	430.21	1	HX8	1494.70	578.23	HX4	225.73	250.00
<i>E-106</i>	19.96	168.34	1	CONDENSER at RECT	64.40	64.04	Cooling Water	20.02	23.00
<i>E-107</i>	9.46	205.76	1	CONDENSER at DISTL	67.81	66.58	Cooling Water	20.02	23.00
<i>E-108</i>	9.31	1828.51	4	REACTOR HEAT	250.00	249.72	HX4	180.80	225.73
<i>E-109</i>	24.87	3131.65	8	HX5	242.95	124.43	HX4	60.82	180.80
<i>E-110</i>	3.52	36.84	1	CONDENSER at DISTL	66.58	66.31	Cooling Water	19.67	20.02
<i>E-111</i>	7.07	481.84	1	REACTOR HEAT	249.72	249.50	REBOILER at DISTL	102.54	103.04
<i>E-112</i>	3.75	68.19	1	HX5	124.43	117.93	REBOILER at RECT	65.71	66.05
<i>E-113</i>	2.25	27.30	1	CONDENSER at RECT	64.04	60.25	Cooling Water	19.44	19.67
<i>E-114</i>	24.95	2248.31	6	HX5	117.93	67.44	HX6	30.28	86.80
<i>E-115</i>	2.19	559.13	2	HX8	578.23	120.00	HX4	50.28	60.82
<i>E-116</i>	0.78	184.86	1	HX5	67.44	64.89	HX4	46.52	50.28
<i>E-117</i>	0.95	293.65	1	HX2	119.66	38.00	Cooling Water	19.08	19.44
<i>E-118</i>	0.62	371.96	1	HX1	93.01	38.00	Cooling Water	19.08	19.44
<i>E-119</i>	0.99	33.36	1	HX7	60.25	30.00	Cooling Water	19.08	19.44
<i>E-120</i>	0.99	193.03	1	HX3	118.20	38.00	Cooling Water	19.08	19.44
<i>E-121</i>	10.66	455.58	1	HX5	64.89	30.00	Cooling Water	18.00	19.08

Appendix 6

Annual fixed and variable OPEX

Table A9: Annual fixed and variable O&M costs of the methanol plants, million euros

<i>FIXED O&M</i>	<i>10 kt/a</i>	<i>50 kt/a</i>	<i>250 kt/a</i>	<i>10 kt/a with CC unit</i>	<i>50 kt/a with CC unit</i>	<i>250 kt/a with CC unit</i>
<i>Direct labour cost</i>	0.60	0.72	1.08	0.90	1.02	1.38
<i>Admin and general overhead cost</i>	0.18	0.216	0.324	0.27	0.306	0.414
<i>Annual O&M</i>	0.23	0.36	0.77	0.33	0.68	1.78
<i>Insurance</i>	0.08	0.12	0.26	0.11	0.23	0.59
<i>Local taxes and fees</i>	0.08	0.12	0.26	0.11	0.23	0.59
<i>Total fixed O&M</i>	1.16	1.54	2.68	1.72	2.46	4.76
<i>VARIABLE O&M</i>						
<i>CO₂</i>	0.71	3.57	17.85	0	0	0
<i>H₂</i>	6.12	26.89	129.99	6.12	26.89	129.99
<i>Electricity</i>	0.0001	0.0003	0.0013	0.06	0.30	1.50
<i>Cooling water</i>	0.14	0.68	3.40	0.14	0.68	3.40
<i>Steam</i>	0	0	0	0.002	0.008	0.041
<i>Process water</i>	0	0	0	0.012	0.060	0.297
<i>Methanol synthesis catalyst</i>	0.00025	0.00126	0.00633	0.00025	0.00126	0.00633
<i>Total variable O&M</i>	8.13	32.69	153.93	8.07	30.52	140.58