CZECH TECHNICAL UNIVERSITY

FACULTY OF MECHANICAL ENGINEERING

DEPARTMENT OF PROCESS ENGINEERING

Design of containerized technology for emission CO_2 conversion to methanol

Diploma thesis

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ZADÁNÍ DIPLOMOVÉ PRÁCE

I. OSOBNÍ A STUDIJNÍ ÚDAJE

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Vyprojektujte a navrhněte 3D dispozici technologie decentralizovaného konverze emisního CO2 na metanol ve standardním kontejneru - projektování a bilancování v AspenPlus, tvorba 3D dispozice jednotky a aparátových listů instalovaných zařízení, investiční náklady a základní ekonomika provozu.

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Jméno a pracoviště vedoucí(ho) diplomové práce:

doc. Ing. Lukáš Krátký, Ph.D.,   ústav procesní a zpracovatelské techniky   FS

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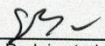| doc. Ing. Lukáš Krátký, Ph.D.	prof. Ing. Tomáš Jirout, Ph.D.	prof. Ing. Michael Valášek, DrSc.
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III. PŘEVZETÍ ZADÁNÍ

Diplomant bere na vědomí, že je povinen vypracovat diplomovou práci samostatně, bez cizí pomoci, s výjimkou poskytnutých konzultací.
Seznam použité literatury, jiných pramenů a jmen konzultantů je třeba uvést v diplomové práci.

18. 5. 2021	
Datum převzetí zadání	Podpis studenta

DECLARATION

I hereby declare that this diploma thesis is my own work and effort and all sources and other materials used have been quoted in the list of references.

In Prague on

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                                                                    signature

Annotation sheet

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Annotation - Czech: Cílem této diplomové práce je vytvořit parametrický simulační model procesu katalytického syntézy metanolu v programu AspenPLUS a navrhnout na základě jeho výsledků small-scale výrobní linku, která se vejde do standartního kontejneru. Součástí práce je i rešeršní část a základní ekonomická bilance.

Annotation - English: The goal of this diploma thesis is to create a parametric process simulation model of catalytic methanol synthesis in AspenPLUS and to design a small-scale methanol synthesis plant based on the simulation results, that would fit into a standard container. A research part and a brief economic analysis is also included.

Keywords: carbon dioxide conversion, methanol, hydrogen, small scale plant, container, process simulation

Acknowledgement

Contents

List of physical quantities

C	capital cost of equipment	[€]
C_d	design factor capital cost	[€]
C_n	construction capital cost	[€]
c_p	specific heat capacity	[J·kg^{-1}·K^{-1}]
C_r	reserve capital cost	[€]
C_{total}	total capital cost	[€]
D	diameter	[m]
H	height	[m]
Δh_g^{sl}	heat of formation	[kJ·mol^{-1}]
ΔH_r^0	standard heat of reaction	[kJ·mol^{-1}]
ΔH_r^T	temperature specific heat of reaction	[kJ·mol^{-1}]
L	length	[m]
M	molar weight	[kg/mol]
$\dot{m}$	mass flow rate	[kg h^{-1}]
$\dot{m}_L$	mass flow rate of liquid in column	[kg s^{-1}]
$\dot{n}$	molar flow	[kmol·h^{-1}]
n_T	number of tubes	[-]
p	pressure	[bar]
$\dot{Q}$	heat capacity	[kW]
R	molar gas constant	[kJ·K^{-1}·kmol^{-1}]
S	area	[m]
T	temperature	[°C]
u	speed	[m·s^{-1}]
$\dot{V}$	volume flow rate	[m^3·h^{-1}]
V_p	volume of pores	[m^3]
W	power	[W]
x	molar concentration	[-]
X	conversion	[-]
ε	porosity	[-]
κ	Poisson's ratio	[-]
μ_L	dynamic viscosity of liquid phase	[Pa·s]
ρ	density	[kg·m^{-3}]
τ	residence time	[s]

φ	stoichiometric coefficient	[-]
Φ_L	flow intensity of liquid phase	[kg·m^{-1}·s^{-1}]

List of shortcuts

RWGS	reverse water gas shift
NOx	nitrogen oxides
TON	turnover number
IMC	intermetallic compound
BWR	boiling water reactor
GHSV	gas hourly space velocity
CAMERE	catalytic methanol synthesis via reverse water gas shift
PFD	process flow diagram
HETP	Height Equivalent to a Theoretical Plate
EUA	European Union allowance

Introduction

It is well documented at this stage, that the CO_2 content in the atmosphere has risen massively since the pre-industrial days and it keeps on rising. Therefore, the motivation for studying the CO_2 to methanol conversion process is to find a way of using the CO_2, that we produce and convert it into something useful. Conversion of CO_2 to methanol is one of four pathways to produce renewable methanol as it was characterised by Law et al in 2013. All of those pathways consist of catalytic conversion technology, the difference being the source of conversion - municipal waste, industrial waste, biomass and CO_2. The first three sources utilize the process of gasification technology, the last one, which theoretically would be our case, uses renewable electricity to produce hydrogen from water. The reason for it being just in the realm of theory in our case is that this thesis will focus strictly on the conversion process and will only take the final products of the CO_2 capturing and H_2 production processes into account.

Methanol has a wide range of utilisations. There is a possibility to use it as a fuel, which would once again lower the use of fossil fuels and therefore the motivation for this process would come full circle.

The way that methanol is now most commonly produced is by hydrogenation of CO, this process has a major drawback from the ecological standpoint, because it relies on hydrogen produced by steam reforming of natural gas, which is a process that in one of the stages requires heating by combustion of fossil fuels. With direct conversion of CO_2 to methanol we get rid of this stage and therefore we meet the demands of our motivation.

To sum up all the previous points, the ideal hypothetical, renewable methanol production process, would be as follows. CO_2 is captured at its source before it even reaches the atmosphere. It could even be stored. Meanwhile hydrogen is produced by electrolysis, using renewable electricity. These two chemicals will then be the two reactants of the reaction, that will have methanol as its product. That end product will then be used as a fuel to further decrease the impact of fossil fuels.

The goals of this diploma thesis are to create a general parametric simulation model in AspenPLUS of the previously described process of CO_2 to methanol conversion followed by its implementation when designing a real disposition-limited process unit.

THEORETICAL PART

The theoretical part of this thesis will be dedicated to an introduction of the chemical reaction and an overview of the research and application in literature. Based on that a block diagram and the process conditions will be defined.

1. CO_2 to methanol basics

This chapter is a brief introduction to the studied chemical reaction.

1.1. CO_2

CO_2 is a colourless gas, that in the solid state is referred to as dry ice. CO_2 sublimes at the temperature of $-78.5\,°C$, at atmospheric pressure. CO_2 is represented in the atmosphere by 0,04 % by volume [1]. Chemically its molecule consists of one atom of carbon and two atoms of oxygen. Both bonds between the carbon and oxygen atoms are double bonds. CO_2 is also produced in nature, for example by volcanoes, hot springs and it also occurs in water as well as in petroleum or natural gas. It is also produced by the process of fermentation. In its solid state we use it as a cooler in food, medical or construction industries.

1.2.   Methanol

Methanol is a colourless liquid, with a boiling point at 64,7 °C. It is sometimes referred to as wood alcohol [2]. It is the simplest alkanol which are alcohols with all bonds between atoms being single bonds. Effectively it is a methyl group linked with a hydroxyl group. A molecule of methanol consists of one atom of carbon, four atoms of hydrogen and one atom of oxygen. The chemical formula of methanol is CH_3OH. There are some hazards associated with methanol, firstly it is flammable and the second is its toxicity. It may cause blindness and cause damage to the kidney, liver and heart in case of swallowing.

There are many ways of application for methanol. Methanol is converted to formaldehyde which is widely used in production of plastics. Acetic acids and other chemicals are also converted from methanol. Methanol is used as an additive to gasoline or as a fuel on its own. It has some good properties as a fuel such as high-octane number, which is an important value for petrol engines and it burns cleaner than gasoline or diesel, the emissions of CO, CO_2, NOx and particulate matter are lower. The complete comparison of properties can be seen in Picture 1 below.

In China, there has been political pressure to use neat methanol fuel "M100" as part of the strategy to reduce carbon emissions, the downside is, that almost all of the methanol in China is produced by steam reforming, so the actual accomplishment of that goal can be disputed. In the US, as well as in other parts of the world, methanol is blended to gasoline for a number of years, in the ratio up to 15 %.

The properties of methanol, gasoline and diesel.

Fuel property	Methanol	Gasoline	Diesel
Formula	CH_3OH	C_{5-12}	C_{10-26}
Molecular weight	32	95–120	180–200
Oxygen content	50%	0	0
Stoichiometric air/fuel ratio	6.45	14.6	14.5
Low calorific value (MJ/kg)	19.66	44.5	42.5
High calorific value (MJ/kg)	22.3	46.6	45.8
Freezing point (°C)	−98	−57	−1 to −4
Boiling point (°C)	64.8	30–220	175–360
Flash point (°C)	11	−45	55
Auto-ignition temperature (°C)	465	228–470	220–260
Research octane number	108.7	80–98	
Motor octane number	88.6	81–84	
Cetane number	3	0–10	40–55
inflammability limit	6.7–36	1.47–7.6	1.85–8.2
specific heat (20 °C) (kJ/kg K)	2.55	2.3	1.9
latent heat (kJ/kg)	1109	310	270
Viscosity (20 °C) (CP)	0.6	0.29	3.9

Picture 1 Properties of methanol, gasoline and diesel [23]

Most commonly it is produced by syngas synthesis. Syngas is a mixture of gases, where the two main components are hydrogen and CO. Very often a smaller amount of CO_2 is also present in the mixture [3]. The reaction exothermically proceeds according to equation (1) below at high pressure and moderate temperatures [2]:

$$CO + 2H_2 \rightarrow CH_3OH \tag{1}$$

1.3. Hydrogen [4]

Hydrogen is a mostly gaseous colourless element. It has three isotopes the most common one being protium, which has one proton, one electron and no neutrons. It is used mostly in petrochemical industry or for example as a cooler.

There are several ways of obtaining pure hydrogen. The most common industrial way is by steam reforming of natural gas (which mainly consists of methane).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{2}$$

The problem with this process is that as part of the process we heat by combustion of natural gas, so we produce a lot of CO_2 by doing it.

A different way of obtaining pure hydrogen is by electrolysis of water.

$$2H_2O \rightarrow 2H_2 + O_2 \tag{3}$$

The environmental side of the process could be questioned, it depends on a set of factors, but the fact that we don't have to use a reformer is a big plus. The biggest drawback of this method is the cost.

Some of the other ways of obtaining pure hydrogen are photochemically or for example by fermentation of biomass.

1.4. Hydrogenation

Hydrogenation is a chemical reaction where the reactants are usually molecular hydrogen (H_2) in gaseous form and one other compound, very often it is an organic compound of some kind. The reaction runs as a synthesis of the hydrogen and the compound. It is used to saturate the compound in the presence of a catalyst of some sort. When saturating an organic compound, you automatically reduce the number of bonds between carbon and hydrogen. The reaction is usually strongly exothermic. The opposite reaction to hydrogenation would be dehydrogenation. The reaction is used mainly in food or petrochemical industry.

1.5. Hydrogenation of CO_2 [5]

In this paper we will be focusing on the conversion of CO_2 to methanol by hydrogenating the CO_2. The product of this reaction will next to the methanol be water. The full chemical equation of this process is:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^0_{r298\ K} = -40{,}9 \text{ kJ/mol} \tag{4}$$
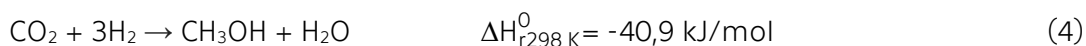
Usually when running this process, two other reactions are happening simultaneously with the first one.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^0_{r298\ K} = 49{,}8 \text{ kJ/mol} \tag{5}$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^0_{r298\ K} = -90{,}7 \text{ kJ/mol} \tag{6}$$
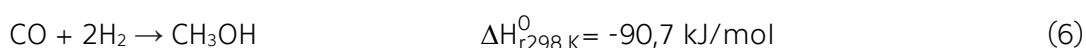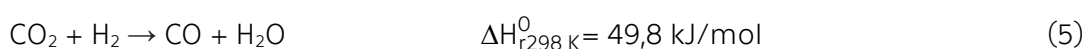
Equation (5) is an undesired reverse water-gas-shift reaction (further referred to as RWGS), that causes a reduction of yield of methanol and furthermore we waste hydrogen with this reaction. Once this reaction occurs some of that CO produced by RWGS again reacts with hydrogen and produces methanol according to equation (6). Because our reaction (4) has a by-product in water, the yield of methanol is lower with this reaction compared to the industrialised production of methanol from syngas. Reactions (4) and (6) are exothermic reactions, reaction (5) on the other hand is an endothermic reaction. The goal is of course to attain the highest yield of methanol from the reaction possible. Some improvements can be attempted by appropriate choice of catalyst, physical conditions, design of the reactor and the overall process.

We can determine the exo/endo-thermicity by evaluating the reactions enthalpy change. We can see that equation (4) and (6) are exothermic, because $\Delta H_r^0 < 0$. Equation (5) however is endothermic because $\Delta H_r^0 > 0$. Due to their exothermicity, equations (4) and (6) will have higher conversion with lower temperature. For endothermic reactions, the opposite applies, therefore for reaction (5) we would get higher conversion with higher temperatures.

The impact of pressure can be evaluated by the sum of stoichiometric coefficients of a reaction. For both reactions (4) and (6) $\Delta \varphi = -2$. When $\Delta \varphi < 0$, with higher pressure, the conversion increases. For reaction (5) $\Delta \varphi = 0$, the amount of substance doesn't change in this reaction and pressure has no impact on conversion.

There are further factors, such as catalyst activity and the overall process design that impact the conversion as well.

2. Methanol synthesis process evaluation

This chapter contains an overview of publications dedicated to this topic and the basic process parameters. Further, three studies are introduced, that implemented the process parameters in practice. After that a more detailed look at the main parameters of the process is taken. The conclusion of this chapter is defining a block diagram, and the key parameters of the chemical reaction based on the previous research.

Only a small number of studies were found, where the process design would go as far as carrying out a practical experiment. The most commonly mentioned experimental study is the study of An et al. from 2009, which studied the reaction conditions for the reaction while using a fibrous Cu/Zn/Al/Zr catalyst. The study of Doss et al. from 2009 also investigated different reaction conditions for methanol synthesis in a cylindrical fixed bed reactor. More recently in the diploma thesis of Laitinen from 2020 an experiment was carried out for a single pass reactor with a commercial Cu/Zn/Al/Mg catalyst. However, most of the studies are only simulation studies, an overview of different studies and the reaction parameters that they implement is in Table 1 below.

No.	patent/publications	simulation/testing results/research/patent	number of reactor stages	catalyst	T [°C]	p [bar]
1	Synthesis of Methanol from Captured Carbon Dioxide Using Surplus Electricity	testing	1	Cu/Mg/Al or Cu/Zn/Al	200-250	20-50
2	Development of an Efficient Methanol Production for Direct CO2 Hydrogenation	simulation	3	Cu/Zn/Al	230	-
3	data of Shiraz Petrochemical Company	testing	-	Cu/Zn/Al	230	-
4	Renewable Methanol Synthesis	research	-	-	-	-
5	Process for the conversion of carbon dioxide to methanol	US9133074, expectations	1	Cu/Zn/Al	220-280	50-100
6	Methanol production process	WO2017140800A1, expectations	1	Cu/Zn/Al	20-300	100-150
7	Methanol and dimethyl ether from renewable hydrogen and carbon dioxide	simulation	2	-	275	17
8	Methanol Production via CO2 Hydrogenation: Sensitivity Analysis and Simulation—Based Optimization	simulation	2	-	183.6	57.8
9	Mixed Metal Oxide Catalysts For Direct CO2 Hydrogenation	WO2017051284A1, expectations	-	-	-	-
10	Continuous Process For Preparation Of Methanol By Hydrogenation Of Carbon Dioxide	WO 2007/108014	-	Cu/Zn/Al	225	50
11	Conversion Of Carbon Dioxide Into Methanol By Hydrogenation	research	-	Cu/Zn/Al	210-270	50-100
12	Methanol synthesis using captured CO2 as raw material	simulation	1	Cu/Zn/Al	210	76
13	Novel efficient process for methanol synthesis by CO2 hydrogenation	simulation	1	Cu/Zn/Al/Zr	250	50
14	Plant To Planet Analysis Of CO2 Based Methanol	simulation	1	Cu/Zn/Al	221–228	50
15	Transformation of Carbon Dioxide into Methanol	simulation	1	Cu/Zn/Al	250	60

Table 1 Process settings overview

2.1. Methanol synthesis flowsheet

The basis of this process is often being reduced into four main steps.

1. Compression
2. Reaction
3. Separation
4. Distillation

The flowsheet according to this basic layout is in Picture 2. In the first phase, both CO_2 and H_2 are compressed, mixed and then heated. This heated mixture is then fed to the reactor, where with the use of the catalyst the reaction takes place. The product of this reaction is cooled, so that it partially condenses. It consists of part liquid phase and part gaseous phase. These phases are separated in the separation vessel, the liquid phase is then heated and continues to the distillation column, where methanol and water are separated, and we get our final products.
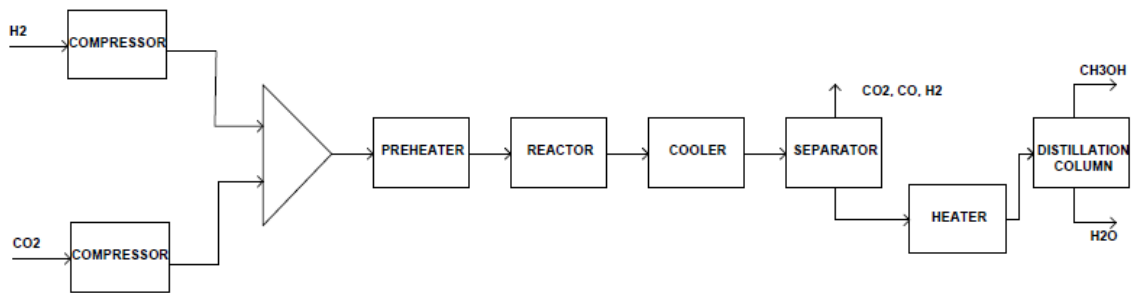
Picture 2 Basic flowsheet

A very common feature, which saves energy and therefore also money, is heat recovery. We can for example use the cooling agent from the cooler before the phase separation vessel and use that heat in the heater on the inlet of the reactor. The same inlet could be fed by recovered heat from the outlet of the reactor, it was already mentioned, that the reaction is exothermic and either way the products must be cooled, before proceeding in the process.

A configuration in which the outlet with the gaseous products from the phase separation vessel is recycled is also applied very often. They are compressed and mixed with the entering CO_2 and H_2 to ensure a higher reactor yield. Another way to use the unreacted gaseous CO_2 and H_2 from the phase separation vessel is to use multiple reactors. This should result in a higher yield, but it is very much an expensive modification. In different numerical simulation studies, it is possible to come across up to three reactors. The problem with this setting is, you would ideally need a separation vessel after each reactor, which is again a big

investment. There is one more reason, why multiple separation vessels would be important as well and that is the need to separate water from the mixture that would be entering any of the reactors, because commercial catalysts do perform worse in the presence of water. Each following reactor usually has a lower yield.

A multiple separation vessel (usually two) after a single reactor approach has also been taken for example in numerical analysis studies of Nieminen et al. [14] or Gonzalez-Garay et al. The first one usually working at higher pressure and the second one at atmospheric pressure. In numerical analysis studies there is often a lot more of purging and separation units throughout the technology, with the focus on the best possible yield of the reaction, however, the financial side of things must be taken into consideration as well and not all of these steps would be feasible.

A slightly different approach was developed at the start of the millennium in South Korea, by the local Institute of Science and Technology. The process was called CAMERE. For this, two reactors were used, the idea was to convert CO_2 to CO by RWGS in the first reactor after that water is removed from the product and the rest of the products proceeded to the second reactor, where methanol synthesis from CO_2 took place. There were claims of higher yield because of the small amount of water in the second reactor, efficiency, and lower cost of this configuration, but those were later declined by the study of Anicic et al., which favoured the direct synthesis in efficiency and cost. [17]

2.2.   Reaction conditions

Three main conditions are assessed with this reaction. Temperature, pressure and H_2 to CO_2 ratio. These are assessed mainly by the selectivity towards methanol and the conversion of the reaction. According to Le Chatelier's principle, it would be safe to assume, that high pressure and low temperature would give us a higher yield. This was also experimentally confirmed.
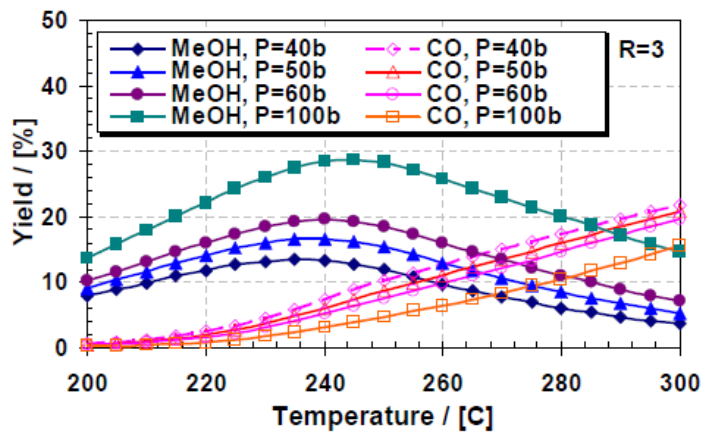
*Picture 3 Effect of temperature on the MeOH and
CO yield, at fixed reactants ratio and various pressures [15]*

The threshold value for temperature is around 300 °C, with increased temperature the selectivity shifts towards CO and further at 300 °C there is a danger of catalyst sintering. From a kinetic perspective however, reaction rate increases with increasing temperature, but at the expense of methanol yield. The conversion of CO_2 to methanol is kinetically limited at low temperatures (to 15 - 25%) and thermodynamically limited at high temperatures. [17] In most studies, the temperature was in the range of 200-280 °C.

As we stated earlier, we can assume, that with higher pressure, we will get higher yield with this reaction. It was experimentally determined that the increase in pressure does not have the negative side effect in equilibrium shift towards RWGS. Where we do get a limitation in choosing pressure values, is the exothermicity of the reaction. The higher pressure we use, the higher yield we get, but the more exothermic heat is produced as well, which gives us some restriction in terms of what our chosen reactor is capable of in cooling. Industrially as well as with most papers that focus on simulation of this process the most common pressure values are in the range from 50 to 100 bars pretty much unanimously.

The last factor which could get us higher yield values if set correctly is the H_2 to CO_2 ratio. Several papers were published, that focused on changing this ratio and what effect that has on the reaction. Our chosen ratio will be a molar ratio of 3,3:1 (H_2:CO_2). In Table 1 is a list of the chosen chemical reaction conditions found in literature.

2.3. Catalysts

A wide range of catalysts has been studied for this reaction, homogenous as well as heterogenous, even some electro (using metals such as Pt, Pd and Ru) and photocatalysts (using oxides such as TiO_2, Cu_2O, CuO and ZnO) but these aren't used very frequently [6]. An overview of the homogenous and heterogenous catalysts and their development in recent years is below.

2.3.1. Homogenous catalysts

There is a relatively small number of studies of homogenous catalysis in comparison to heterogenous, after all it has been only in the last ten years, that some real progress has been made in this branch. Nonetheless there are some clear upsides to using homogenous catalysts instead of heterogenous, the first one being that they are able to operate at lower temperatures (below 150 °C) and pressures than heterogenous catalysts. The overall activity and selectivity of homogenous catalysts is also better than with the heterogenous alternative and finally probably the biggest motivation for pursuing these kinds of catalysts is that there is a potential for a higher yield. There are some drawbacks as well of course, one of the main being the pour ability of recovery and regeneration. [9]

Over the years of developing new catalysts and ways of homogenous catalysis a set of criterias has been continuously forming throughout the process.

The first attempt at using a homogenous catalyst was carried out by Tominiga et al. in 1995. For the experiment molecular hydrogen was used as well as $Ru_3(CO)_{12}$ and potassium iodide in a N-methylpyrrolidone solution. The process had two steps, in the first CO was formed through WGS at around 200 °C than by hydrogenation methanol was formed at around 240 °C under 80 bar of a $3H_2{:}CO_2$ mixture. The process underachieved in terms of selectivity and high operating temperatures. [7]

For those last-mentioned reasons, the next ambition was to run our catalysis in just one step, fast forward to 2011 when Huff and Sanford et al., published a study on cascade catalysis. This enabled a direct synthesis of CO_2 to methanol, but three catalysts had to be used and as expected, the turnover number (further referred to as TON) of this process was very low. The higher number of catalysts was determined to be an unresolvable hurdle and so the next steps of the research went in the direction of reducing the number of catalysts to only one. [7]

Klankermayer, Leitner et al. made big progress by publishing their study in 2012 which regarded the use of tridentate phosphorus ligande, triphos - (1,1,1-

tris(diphenylphosphinomethyl)ethane), with ruthenium as the central metal and an alcohol additive (ethanol), which was able to generate a TON of up to 221. The team later identified the cationic formate complex [(Triphos)Ru(η^2-O_2CH)(S)]$^+$ (S=solvent) as a catalytically active intermediate. This structure later served as the foundation for many studies. With this discovery Klankermayer, Leitner et al. were able to eliminate the use of the alcohol additive and were further able to double the TON to 442, with the use of a co-catalyst bis(trifluoromethane) sulfimide (HNTf$_2$). They even began to work on separating and recycling the catalyst from the product mixture. [7], [10]

It is important to note, that the studies mentioned thus far in this paper, such as the studies of Leitner or Sanford are all operating under acidic conditions. The majority of studies regarding CO_2 capture accomplish it by using basic conditions, therefore some additional processes, such as desorption, would have to take place before we could proceed to the next step of converting the CO_2 in case of operating under acidic conditions. Because of that we would prefer our catalysis to operate under basic conditions as well. [7] The first studies, that were able to realise this (Sanford et al., Ding et al. both in 2015) were able to make the reaction happen, but it came with a price of either not being able to do it in one step which as we stated earlier was not a desired procedure or methanol came just as a by-product, the objective of these wasn't mainly methanol production. It was Prakash, Olaf et al., with the extension of their study from 2015, that were able to realise Ru and Fe based reactions with a methanol yield of 79 %, treated with 50 bars of hydrogen pressure and 155 °C, that was working with CO_2 that was captured directly from the air at basic conditions. They even managed to recycle the catalyst with a total TON of 1850 after the 5th cycle and the products, methanol and water were collected between each cycle by simple distillation. [7]

The next criterion takes mostly the economic standpoint into account. In the early stages of studying homogenous catalysis almost all of the studies used noble metals, most commonly ruthenium, but in some cases also iridium or rhodium. Although the data showed some promising results, it is simply very hard to imagine the use of a noble metal catalyst in a wider range because of the price, so a new desire to discover a non-noble metal homogenous catalyst was developed.

The first non-noble metal catalyst system was discovered in 2017 by Beller et al., it was based on Cobalt and inspired by the aforementioned ruthenium system from 2012 by Leitner. In 2017 Prakash et al. published a study about a sequential hydrogenation process using a Manganium based catalyst. The yield and conditions of the reaction were very promising, but the TON of 36 was an

underwhelming result. In the same year Pombeiro et al. used an iron catalyst and ran the reaction at 80 °C and 75 bars, it is important to notice the relatively high (high in comparison to other CO_2 to methanol processes) TON at 2283. [7]

Overall, there is still a lot of uncharted territory with this topic, as it was already mentioned, the research just started to deliver some more notable methods and results. There is definitely room for improvement, for example the values of TON still haven't reached a very satisfying level. On the other hand, we have reached temperatures as low as 80 °C as well as very low pressure values which in comparison to heterogenous catalysts is a much better result. There were also some attempts at solving the problem with recycling of the catalyst. We are also finally turning in the direction of studying non-noble metal catalysts, and although there are improvements to be made, with using these, there is a chance that it would be applicable in a larger scheme of things.

2.3.2.   Heterogenous catalysts

Although there are some notable distinctions between obtaining methanol through syngas and CO_2 (such as the higher exothermicity of the syngas reaction and the higher production of water with the CO_2 synthesis, which as stated earlier causes a premature deactivation of the catalysts), the overall processes are similar, so firstly it was experimented with the formulas from the syngas reaction. As expected, the yields are lower with the synthesis of CO_2, caused by the previously mentioned reasons as well as the difficult activation of CO_2. Therefore, adjustments are being developed as well as entirely new catalysts. [6]

2.3.2.1.   *Cu-based catalysts*

When talking about drawing inspiration from the syngas synthesis methods, it has been mostly Cu based catalysts in combination with ZnO that have been used for CO_2 synthesis in different variations. The most common is the Cu-ZnO-Al_2O_3 catalyst, typically consisting of 60 wt% Cu, 30 wt% ZnO and 10 wt% Al_2O_3 [11]. The main component is always the metal (in this case Cu), and the oxides are there to enhance the abilities of the main component. Cu when used as a catalyst in this reaction is dependent on surface area, therefore we use ZnO because it enhances the structure as well as the electronic side of things. It increases the surface area and Cu dispersion and modulates the electron properties [11]. There are different methods of applying the compound which drastically affects the final efficiency of the catalyst (shape etc.). Al_2O_3 is used to further increase the structural distribution of Cu and increase the surface area and the mechanical stability of the catalyst

[11]. An important variable in the catalyst activity is the way it is prepared. Cu based catalysts are generally prepared by co-precipitation of salt precursors such as nitrates of Cu, Zn etc. with a basic precipitating agent in an aqueous medium, followed by ageing, calcination and reduction [11]. In case of the $Cu-ZnO-Al_2O_3$ catalyst modifications have been done for this preparation process for example according to Pérez-Ramírez et al., using oxalate precursors results in minimizing the content of residual carbon with which the Cu-ZnO interaction is improved as well as the overall activity of the catalyst. To further improve the $Cu-ZnO-Al_2O_3$ catalyst properties different kinds of promoters have been studied. The first studied promoters are noble metals such as Pt, Rh, Au or Pd which increase the activity of Cu, but this increase of activity cannot justify the cost of these materials and therefore they likely won't be used further than just experimentally. Next there are studies of improvements through the interaction between promoters and Al. In this case, the three most commonly used promoters are Zr, Ga and F. [6] There are some alternatives for Al_2O_3, for example ZrO_2 or CeO_2. CeO_2 showed some promising results, but due to its low stability in large amounts of water it is not very applicable. ZrO_2 has a less hydrophilic character than Al_2O_3, furthermore the use of ZrO_2 results in a higher basicity of the catalyst. It is experimentally proven, that ZrO_2 is the most effective out of these three oxides. There is a big variety in preparation of catalysts with ZrO_2, from reverse co-precipitation, oxalate gel co-precipitation, complexation with citric acid to surfactant-assisted co-precipitation [11].

Another alternative is Ga_2O_3 which is most commonly prepared by ways of co-precipitation and citric acid complexing. Some of the other oxides used are In_2O_3, MgO or TiO_2 [6].

2.3.2.2.   Noble metal-based catalysts

The next most frequently used element after Cu is Pd. It is more stable than Cu, because of its resistance to sintering [11]. The selectivity of Pd is of course given by the choice of promoter and way of preparation. Similarly to Cu based catalysts, oxides are used as promoters (ZnO, Ga_2O_3, CeO_2, In_2O_3, although for example in the case of ZnO, Pd has strong tendencies to form a Pd-Zn alloy, so the actual results for ZnO are questionable [11]), mesoporous silica as well as some carbon materials. As for the ways of preparation, impregnation is the most common, but among others sol-immobilisation, co-precipitation and citrate decomposition are used as well.

The next noble metal on which numerous researches have been made is Au. Gold in the form of nanoparticles has proven to be a highly active catalyst [6]. The best results were achieved with the assistance of the oxide promoter ZnO. It was well documented that Au with the support of ZnO had better results as far as selectivity towards CO_2 than the aforementioned $Cu-ZnO-Al_2O_3$ catalyst. Some good results were achieved also with the promoter CeO_2. On the other hand, while the TiO_2 and Fe_2O_3 promoters showed a high conversion (up to 40%), the conversion happens almost exclusively in the favour of CO and CH_4, so for us they become useless. Al_2O_3 promoters have been studied as well but showed no significant signs of activity. [6] A little bit of research has also been done on Ag, Pt and Re based catalyst, but nothing of big significance came out of these studies [11].

2.3.2.3. Bimetallic catalysts

Thus far we were discussing only monometallic catalysts, so the third group of studied catalysts are bimetallic catalysts (a combination of two or more metals). We could split bimetallic catalysts further in two categories of alloys and intermetallic compounds. The most frequently discussed alloys are Cu-Zn and Pd-Zn. The alloys formed by deep reduction of Cu-ZnO, respectively Pd-ZnO. Pd on its own, leads to formation of only CO through RWGS, meanwhile nanoparticles of the Pd-Zn alloy are selective to methanol [6]. Cu-Pd, Cu-Ag, Cu-Ni, Pd-Ga, Pt-Co, and Rh-W were studied as well. The typical preparation methods are similarly to previous catalysts, impregnation, co-precipitation, sol-immobilisation etc.

As for the intermetallic compounds, they have also shown some significant activity and methanol selectivity for CO_2 hydrogenation, particularly Pd-Ga, Pd-Zn, Pd-In, Cu-In and Ni-Ga IMCs [11]. Typical preparation methods are impregnation and co-precipitation, oxides such as Ga_2O_3, MgO and SiO_2 have been used to support the IMCs.

2.3.2.4. Oxide catalysts

Oxides are used as such on their own or as hybrid oxides catalysts. In_2O_3 has proven to have good catalyst qualities, with good selectivity and stability. There have been researches that achieved improvements when using Pd and Co as promoters. Indium oxides have also been used as oxides hybrids as In_2O_3/ZrO_2 and have shown very good results. Other oxide hybrids such as ZnO/ZrO_2 have also been studied. In ways of preparation there are no different, than the previous catalysts, they are prepared mostly by ways of impregnation or co-precipitation.

2.4. Reactor design

The main hurdle in designing a reactor for this reaction is the exothermicity of the reaction. We need to be able to remove the excess exothermic reaction heat from the process, so that the equilibrium of the reaction is not shifted, and the catalyst is not harmed, which would lead to its deactivation. [17] As is the case with all aspects of this process, the main inspiration is always drawn from the more developed syngas methanol synthesis process. The most common solution for that process is the boiling water tubular reactor (BWR). However due to the lesser exothermicity of this hydrogenation process, the BWR configuration will not be necessary. Moreover, in large scale tubular reactors a hollow section in the centre of the reactor is needed in tubular reactors to support the weight of the catalyst, providing additional mechanical structures or supports. This has a negative effect on the reactor performance, for small scale units this kind of support is not required. [18] There are three most common reactor designs, that are being used where the first two are dominant. Lurgi's reactor, the conventional ICI reactor and the third one is the Kellog and Holdor Topsoe's reactor. A basic sketch of all three reactors is in Picture 4.

2.4.1. Lurgi's reactor [19]

It is an expensive but effective choice. It is a tubular reactor. The tubes are packed with the catalyst, and they are cooled indirectly. The temperature of the water can be easily regulated by pressure. There are a handful of variations of this reactor, but the basis of cooling is always the same. With this, near isothermal process can be achieved and further the temperature profile is even, which has a good effect mainly on the performance (good conversion rates) and longevity of the catalyst. The temperature can be held low, therefore there is a lesser danger of sintering, due to this fact, the catalyst life can be as long as 5 years. The main negative of this reactor is its high investment cost, because of its complex mechanical design.

2.4.2. ICI reactor [19]

This reactor was developed by ICI Synetix which was later sold to Johnson Matthey. It is a series quench reactor, which consists of several adiabatic catalyst beds installed in series. The cooling is done internally and directly, the cooling agent in this case is the feed gas, which is fed into each chamber. Unlike Lurgi's reactor, the ICI reactor is relatively cheap, but it doesn't get nearly as good results as the tube reactor. The dilution of the feed gas plays a major role in these results. Because of

the design a part of the feed gas travels only through part of the reactor and therefore some of the catalyst is underutilised and it reacts inhomogenously which results in a higher formation of by-products. To achieve a good result in conversion, we would have to connect several reactors in series.

2.4.3.   Kellog and Holdor Topsoe's reactor [19]

It's again a series adiabatic reactor, the difference is that the Kellog and Holdor Topsoe reactor uses interstage cooling. It also has an improved design, so it is able to withstand higher pressure, which leads to thinner walls and therefore lower cost.
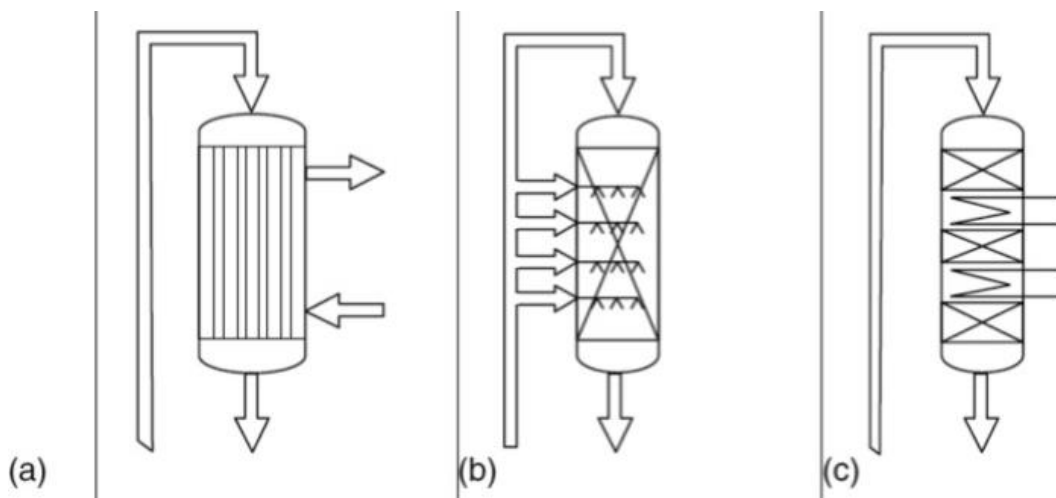
Picture 4 Reactor designs [19]

2.5.   Methanol plants in use

Although the conditions for willingness to fund the research in this field from the authorities are good due to political/environmental reasons, there is only one company that was able to actually convert it into a functioning commercial scale plant.

2.5.1.   CRI plant Svartsengi

It is the first commercial scale renewable methanol plant in the world, situated in the geothermal power plant in Reykjanes, Iceland. It is in some cases also called the George Olah Plant, named after the founding father of the idea to utilize this process, who even got a Nobel prize for the inventions in this field. The plant started operating in 2012, it produces the greenest methanol in the world and

reduces the carbon emissions by 90 % in comparison to methanol, that is produced using fossil fuels. Electrolysis of water is used to produce hydrogen and a modified Lurgi's reactor is used. CRI (Carbon Recycling International, founded in 2006), the company, that runs this project since than is looking to further expand with this technology.

2.6. Methanol synthesis process proposal

The main components and conditions of methanol synthesis were evaluated in this chapter based on research in literature. To sum it up, below are the main conclusions from the research.

The conditions for our reaction should be set as follows:

- the operating temperature of the chemical reaction should be in the range of $200 - 280\,°C$
- the operating pressure of the chemical reaction should be in the range of $50 - 100$ bar
- the molar ratio of H_2 to CO_2 should be 3,3:1

Although there has been a lot of papers published with novel catalysts, with some promising alternatives to the conventional $Cu-ZnO-Al_2O_3$ catalyst, after researching commercial catalysts, that are available on the market as well as from further research of this topic, it was clear, that across the board the conventional $Cu-ZnO-Al_2O_3$ catalyst is the only available option.

Lurgi's reactor has been assessed as the best suited for this process.

Below is a proposed block diagram (Picture 5), based on the research.
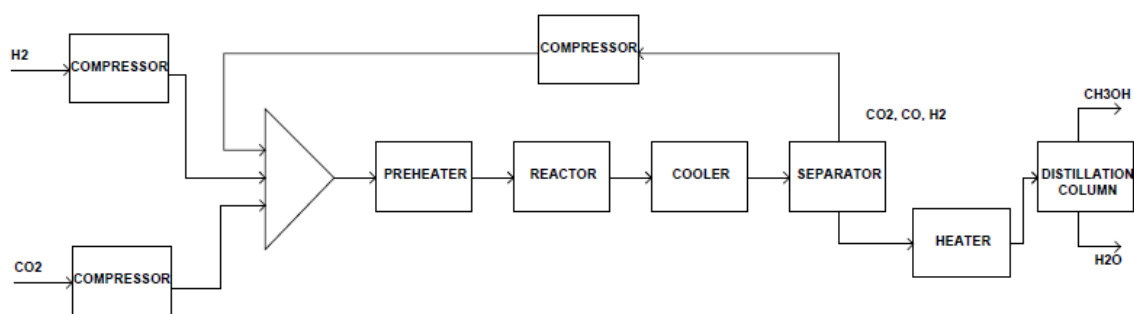
Picture 5 Proposed flowsheet

PRACTICAL PART

The aim of the practical part of the thesis is to create a parametric model in AspenPLUS, which further consists of defining process conditions based on the previous research, creating a PFD and successfully running the simulation. After that a capacity implementation of the technology to a standard container using the parametric model is done. A 3D disposition model is created, and the used equipment is characterised and finally an economical analysis of operational and capital cost is done.

A number of assumptions were made in the practical part of this thesis.

- The law of conservation of mass applies.

$$\dot{m}_{IN} = \dot{m}_{OUT} \qquad (7)$$

- The law of conservation of energy applies.

$$\dot{Q}_{IN} = \dot{Q}_{OUT} \qquad (8)$$

- We neglect heat loss and pressure drop.
- We assume 100% purity of the inlet gases.

3. Parametric model in AspenPLUS

The aim of this section is to create a functioning parametric simulation model for this process. A PFD was set up in AspenPLUS, based on the previous research and the proposed block diagram (Picture 5). The inlet chemicals are mixed with the recycle stream (block MIX1) and the mixture compressed to 100 bar. The compressed mixture is then heated in a heat exchanger to 225 °C (block PREHEAT) and after that it enters the reactor (block REACTOR). The products are then used as a heating medium in the PREHEAT block and after that the product mixture is cooled in a heat exchanger (block COOLER) with water as the cooling medium. The mixture is cooled to 35 °C and it enters the separator where the mixture expands – the pressure drops down to 5 bar, and the phases are separated. The gaseous phase is recycled and a 2% purge stream splits in the SPLITTER block. The liquid phase from the separator is heated to 64,7 °C (block HEATER) and then methanol and water are separated in the distillation column (DIST block). The characteristic process conditions are summarized in Table 2 below.

Reaction operating temperature	255 °C
Reaction operating pressure	100 bar
H_2:CO_2 molar ratio	3,3:1

Table 2 Characteristic process conditions

The PFD is in Picture 6 below.

The entrance flowrates for the parametric model were chosen randomly since this is a default model. The flowrate values are in Table 3.

H_2	100 kg/h
CO_2	660 kg/h

Table 3 Entrance flowrates

A description and set up for each main apparatus simulation model is presented with the results below.
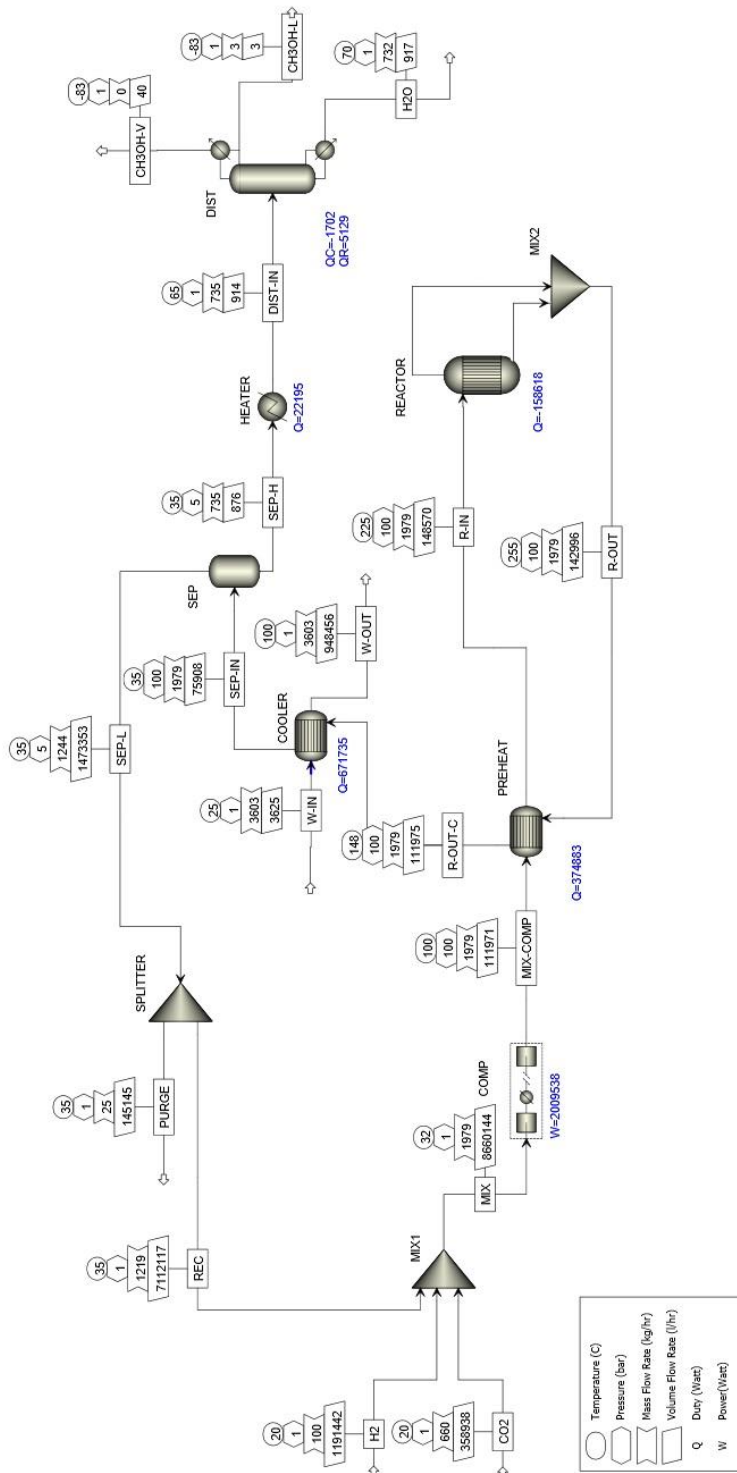
Picture 6 Parametric model AspenPLUS PFD

3.1. Compressor

A multistage compression model MCompr is used for the simulation. This model represents a multistage centrifugal compressor. The model is set up so that we compress the gas mixture to 100 bar. Interstage cooling is implemented, so that we don't get over the 200 °C threshold. Below are the results for this simulation block.

```
BLOCK:  COMP    MODEL: MCOMPR
------------------------------
INLET STREAMS:       MIX              TO STAGE  1
OUTLET STREAMS:      MIX-COMP         FROM STAGE  8
```

```
             *** MASS AND ENERGY BALANCE ***
                         IN               OUT              RELATIVE DIFF.
TOTAL BALANCE
MOLE (KMOL/HR)          345.619          345.619          0.00000
MASS (KG/HR)            1978.52          1978.52          -0.114921E-15
ENTHALPY (WATT)         -0.310752E+07    -0.290721E+07    -0.644619E-01
```

```
             *** CO2 EQUIVALENT SUMMARY ***
FEED STREAMS CO2E            990.687    KG/HR
PRODUCT STREAMS CO2E         990.687    KG/HR
NET STREAMS CO2E PRODUCTION  0.00000    KG/HR
UTILITIES CO2E PRODUCTION    0.00000    KG/HR
TOTAL CO2E PRODUCTION        0.00000    KG/HR
```

```
              *** INPUT DATA ***
ISENTROPIC CENTRIFUGAL COMPRESSOR
NUMBER OF STAGES                 8
```

```
              *** RESULTS ***
FINAL PRESSURE,         BAR             100.000
TOTAL WORK REQUIRED,    WATT            2,009,540.
TOTAL COOLING DUTY ,    WATT            -1,809,220.
```

3.2. Preheater

The HeatX block is used for the heat exchanger simulation. The cold side medium is the compressed gas mixture, and it is heated from 100 °C to 255 °C. The hot side medium is the products of the chemical reaction, and they are cooled from 255 °C to 148 °C. The flow direction is set up as counter current.

```
BLOCK:  PREHEAT  MODEL: HEATX
-----------------------------
HOT SIDE:
  ---------
INLET STREAM:                R-OUT
OUTLET STREAM:               R-OUT-C
COLD SIDE:
  ----------
INLET STREAM:                MIX-COMP
```

OUTLET STREAM: R-IN

                    *** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (KMOL/HR)	661.836	661.836	0.00000
MASS (KG/HR)	3957.03	3957.03	0.00000
ENTHALPY (WATT)	-0.559814E+07	-0.559814E+07	0.00000

                    *** CO2 EQUIVALENT SUMMARY ***

FEED STREAMS CO2E	1332.85	KG/HR
PRODUCT STREAMS CO2E	1332.85	KG/HR
NET STREAMS CO2E PRODUCTION	0.00000	KG/HR
UTILITIES CO2E PRODUCTION	0.00000	KG/HR
TOTAL CO2E PRODUCTION	0.00000	KG/HR

FLOW DIRECTION AND SPECIFICATION:
COUNTERCURRENT   HEAT EXCHANGER
SPECIFIED COLD OUTLET TEMP
SPECIFIED VALUE   C   225.0000
LMTD CORRECTION FACTOR   1.00000

PRESSURE SPECIFICATION:
HOT SIDE OUTLET PRESSURE   BAR   100.0000
COLD SIDE PRESSURE DROP   BAR   0.0000

                 *** OVERALL RESULTS ***
STREAMS:
```
            -------------------------------------
                  |                 |
R-OUT   ----->|        HOT        |-----> R-OUT-C
T= 2.5500D+02 |                   |   T= 1.4780D+02
P= 1.0000D+02 |                   |   P= 1.0000D+02
V= 1.0000D+00 |                   |   V= 9.7726D-01
                  |                 |
R-IN    <-----|        COLD       |<----- MIX-COMP
T= 2.2500D+02 |                   |   T= 1.0000D+02
P= 1.0000D+02 |                   |   P= 1.0000D+02
V= 1.0000D+00 |                   |   V= 1.0000D+00
            -------------------------------------
```
DUTY:
CALCULATED HEAT DUTY   WATT   374882.6850

3.3. Reactor

There are two main objectives of simulating a chemical reactor. The first is to determine the composition of the products of the chemical reaction for the given conditions. The second is determining the residence time which is the key parameter when designing a reactor. We can obtain the residence time only when using a kinetically controlled reactor, when using the thermodynamic pathway alternative, residence time must be calculated separately.

In addition, this simulation can give us some idea about the cooling in case of an exothermic reaction and heating in case of an endothermic reaction, that is necessary in the reactor.
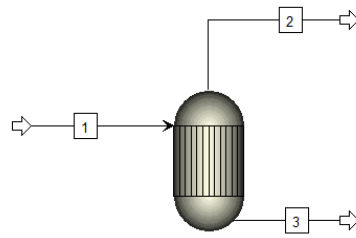
Picture 7 Reactor block REquil

3.3.1.   Kinetic vs Thermodynamic Control

One of the things, that need to be determined going into the simulation in AspenPLUS is whether the reaction is controlled by kinetic or thermodynamic factors. Depending on the pathway the reaction can have a different outcome. This is hard to determine without an actual experiment so we will have to base this on data from other studies. In the study of Shachit et al. the equilibrium-based approach and the rate based-approach are compared. For the isothermic conditions at inlet temperatures beyond 246,85 °C, the conversion of the kinetic model matches with that of the thermodynamic model. It is however important to note, that the composition of reactor inlet does not match to our case. No other study that would match our inlet composition was found, therefore we adopted the assumption, that for higher temperatures, the rate and equilibrium-based simulation results are similar. In other simulation-based studies of this process for various reaction conditions both types of reactor controls were utilised.

The kinetically controlled reactor block used in AspenPLUS is the RPlug reactor block. This model requires information depending on the type of reactor we choose (specific temperature, adiabatic or cooled) and depending on the type chosen, the required specifications vary. Information about the catalyst can be specified as well. [20] Unlike with the equilibrium-based block models, complex information about the reaction kinetics is demanded. For this reason, setting up the RPlug reactor can be a very complicated procedure.

The alternative is the REquil block, which is one of the equilibrium-based reactor model blocks offered by AspenPLUS (Picture 7) and it was chosen as the best suited for this simulation. Setting up this block is much easier than the RPlug block, only information about temperature, pressure and the chemical reactions

stoichiometry is required. This was also the deciding factor in choosing this reactor block for this simulation.

The REquil reactor has one inlet stream and two outlet streams for the liquid and gas phase of the reaction product. In our case, the two outlet streams are mixed right after the reactor into stream R-OUT which represents the complete chemical reaction product outlet stream.

BLOCK: REACTOR MODEL: REQUIL

INLET STREAM: R-IN
OUTLET VAPOR STREAM: 4
OUTLET LIQUID STREAM: 5

        *** MASS AND ENERGY BALANCE ***

	IN	OUT	GENERATION	RELATIVE DIFF.
TOTAL BALANCE				
MOLE (KMOL/HR)	345.619	316.217	-29.4023	0.00000
MASS (KG/HR)	1978.52	1978.52		-0.706328E-11
ENTHALPY (WATT)	-0.253232E+07	-0.269094E+07		0.589450E-01

        *** CO2 EQUIVALENT SUMMARY ***
FEED STREAMS CO2E	990.687	KG/HR
PRODUCT STREAMS CO2E	342.162	KG/HR
NET STREAMS CO2E PRODUCTION	-648.524	KG/HR
UTILITIES CO2E PRODUCTION	0.00000	KG/HR
TOTAL CO2E PRODUCTION	-648.524	KG/HR

        *** INPUT DATA ***
TWO   PHASE TP FLASH
SPECIFIED TEMPERATURE C   255.000
SPECIFIED PRESSURE   BAR   100.000
MAXIMUM NO. ITERATIONS   30
CONVERGENCE TOLERANCE   0.000100000
LIQUID ENTRAINMENT   0.0000
SOLID SPLIT FRACTIONS:
SUBSTREAM NO. =   1 MIXED SUBSTREAM, NO SOLID SPLITS.

        *** RESULTS ***
OUTPUT TEMPERATURE   C   255.00
OUTPUT PRESSURE   BAR   100.00
HEAT DUTY   WATT   -0.15862E+06
VAPOR FRACTION   1.0000

REACTION EQUILIBRIUM CONSTANTS:

REACTION NUMBER	EQUILIBRIUM CONSTANT	EQUILIBRIUM TEMPERATURE	TEMPERATURE UNIT
1	0.20833E-04	255.00	C
2	83.391	255.00	C

3.4. Cooler

This heat exchanger is again simulated by the HeatX block. The hot side medium are the products of the chemical reaction, and they are cooled from 148 °C to 35 °C. The cold side medium is water, and it is heated from 25 °C to 100 °C. The flow direction is set up as counter current.

BLOCK: COOLER   MODEL: HEATX

```
------------------------------
```

HOT SIDE:
```
  ---------
```

INLET STREAM:	R-OUT-C
OUTLET STREAM:	SEP-IN

COLD SIDE:
```
  ----------
```

INLET STREAM:	W-IN
OUTLET STREAM:	W-OUT

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (KMOL/HR)	516.216	516.216	0.00000
MASS (KG/HR)	5581.57	5581.57	0.00000
ENTHALPY (WATT)	-0.189437E+08	-0.189437E+08	0.00000

*** CO2 EQUIVALENT SUMMARY ***

FEED STREAMS CO2E	342.159	KG/HR
PRODUCT STREAMS CO2E	342.159	KG/HR
NET STREAMS CO2E PRODUCTION	0.00000	KG/HR
UTILITIES CO2E PRODUCTION	0.00000	KG/HR
TOTAL CO2E PRODUCTION	0.00000	KG/HR

*** INPUT DATA ***

FLOW DIRECTION AND SPECIFICATION:

COUNTERCURRENT   HEAT EXCHANGER

SPECIFIED HOT OUTLET TEMP

SPECIFIED VALUE	C	35.0000
LMTD CORRECTION FACTOR		1.00000

PRESSURE SPECIFICATION:

HOT SIDE OUTLET PRESSURE	BAR	100.0000
COLD SIDE PRESSURE DROP	BAR	0.0000

*** OVERALL RESULTS ***

STREAMS:

```
          --------------------------------------
                |                    |
R-OUT-C ----->|        HOT          |-----> SEP-IN
T= 1.4780D+02 |                     |     T= 3.5000D+01
P= 1.0000D+02 |                     |     P= 1.0000D+02
V= 9.7726D-01 |                     |     V= 8.6964D-01
                |                    |
W-OUT  <-----|        COLD         |<----- W-IN
T= 1.0002D+02 |                     |     T= 2.5000D+01
```

P= 1.0132D+00 | | P= 1.0132D+00

V= 1.5544D-01 | | V= 0.0000D+00

DUTY:

CALCULATED HEAT DUTY   WATT   671735.3739

3.5.   Separator

The block Flash2 was used for the separator, which is a flash vapour-liquid separator. It has one inlet and two outlets, as is shown in Picture 8 below, one for the vapour phase and one for the liquid phase. Only two variables need to be set up to run this block, these are optional, in our case they are temperature and pressure. The temperature is set up to 35 °C and the pressure to 5 bar.
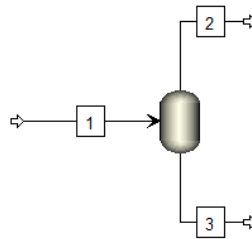
Picture 8 Flash2 simulation block

BLOCK: SEP   MODEL: FLASH2

INLET STREAM: SEP-IN

OUTLET VAPOR STREAM: SEP-L

OUTLET LIQUID STREAM: SEP-H

          *** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (KMOL/HR)	316.216	316.216	-0.179761E-15
MASS (KG/HR)	1978.51	1978.51	0.114922E-14
ENTHALPY (WATT)	-0.373755E+07	-0.363399E+07	-0.277071E-01

          *** CO2 EQUIVALENT SUMMARY ***

FEED STREAMS CO2E	342.159	KG/HR
PRODUCT STREAMS CO2E	342.159	KG/HR
NET STREAMS CO2E PRODUCTION	0.00000	KG/HR
UTILITIES CO2E PRODUCTION	0.00000	KG/HR
TOTAL CO2E PRODUCTION	0.00000	KG/HR

          *** INPUT DATA ***

TWO   PHASE TP FLASH

SPECIFIED TEMPERATURE C   35.0000

SPECIFIED PRESSURE   BAR   5.00000

MAXIMUM NO. ITERATIONS   30

CONVERGENCE TOLERANCE   0.000100000

          *** RESULTS ***

OUTLET TEMPERATURE   C   35.000

OUTLET PRESSURE   BAR   5.0000

HEAT DUTY	WATT	0.10356E+06
VAPOR FRACTION		0.90724

3.6. Heater

The block model Heater is used for the heater that heats up the mixture on the inlet of the distillation column. Two parameters need to be set up for the block, these are optional, in our case they are temperature and pressure. Temperature is set up to 64,7 °C and pressure to 1,01325 bar.

```
BLOCK: HEATER  MODEL: HEATER
------------------------------
INLET STREAM:      SEP-H
OUTLET STREAM:     DIST-IN
```

*** MASS AND ENERGY BALANCE ***			
	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (KMOL/HR)	29.3312	29.3312	0.00000
MASS (KG/HR)	734.996	734.996	0.154677E-15
ENTHALPY (WATT)	-0.213909E+07	-0.211743E+07	-0.101253E-01

*** CO2 EQUIVALENT SUMMARY ***		
FEED STREAMS CO2E	4.90096	KG/HR
PRODUCT STREAMS CO2E	4.90096	KG/HR
NET STREAMS CO2E PRODUCTION	0.00000	KG/HR
UTILITIES CO2E PRODUCTION	0.00000	KG/HR
TOTAL CO2E PRODUCTION	0.00000	KG/HR

*** INPUT DATA ***		
TWO PHASE TP FLASH		
SPECIFIED TEMPERATURE	C	64.7000
SPECIFIED PRESSURE	BAR	1.01325
MAXIMUM NO. ITERATIONS		30
CONVERGENCE TOLERANCE		0.000100000

*** RESULTS ***		
OUTLET TEMPERATURE	C	64.700
OUTLET PRESSURE	BAR	1.0132
HEAT DUTY	WATT	21659.
OUTLET VAPOR FRACTION		0.23052E-06

3.7. Distillation column

To simulate the distillation column, we followed a well-established procedure, first the DSTWU distillation column block is simulated. This simulation model however just gives us input values for the RadFrac distillation column block, which replaces the DSTWU block in step two. The RadFrac simulation block gives us the real outlet stream composition. To successfully run the simulation with the RadFrac block, information about the number of stages, condenser, reboiler and pressure need to be filled in. Also, some further operating, and stream specifications are demanded.
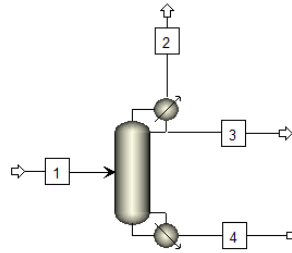
Picture 9 RadFrac simulation block

BLOCK: DIST   MODEL: RADFRAC

INLETS -   DIST-IN   STAGE 5
OUTLETS -   CH3OH-V   STAGE 1
                               CH3OH-L   STAGE 1
                               H2O   STAGE 9

        *** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (KMOL/HR)	29.3312	29.3312	0.00000
MASS (KG/HR)	734.996	734.996	-0.111150E-08
ENTHALPY (WATT)	-0.211743E+07	-0.210175E+07	-0.740507E-02

        *** CO2 EQUIVALENT SUMMARY ***

FEED STREAMS CO2E	4.90096	KG/HR
PRODUCT STREAMS CO2E	4.90096	KG/HR
NET STREAMS CO2E PRODUCTION	0.234399E-05	KG/HR
UTILITIES CO2E PRODUCTION	0.00000	KG/HR
TOTAL CO2E PRODUCTION	0.234399E-05	KG/HR

   **** INPUT PARAMETERS ****

NUMBER OF STAGES	9
ALGORITHM OPTION	STANDARD
ABSORBER OPTION	NO
INITIALIZATION OPTION	STANDARD
HYDRAULIC PARAMETER CALCULATIONS	NO
INSIDE LOOP CONVERGENCE METHOD	BROYDEN
DESIGN SPECIFICATION METHOD	NESTED
MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS	25
MAXIMUM NO. OF INSIDE LOOP ITERATIONS	10
MAXIMUM NUMBER OF FLASH ITERATIONS	30
FLASH TOLERANCE	0.000100000
OUTSIDE LOOP CONVERGENCE TOLERANCE	0.000100000

   **** COL-SPECS ****

MOLAR VAPOR DIST / TOTAL DIST	0.030000
MOLAR REFLUX RATIO	1.01929
MOLAR DISTILLATE RATE KMOL/HR	14.9310

   **** PROFILES ****

P-SPEC   STAGE 1 PRES, BAR   1.01325

```
  ***   SUMMARY OF KEY RESULTS   ***
TOP STAGE TEMPERATURE            C              61.2505
BOTTOM STAGE TEMPERATURE         C              94.5681
TOP STAGE LIQUID FLOW            KMOL/HR        15.2191
BOTTOM STAGE LIQUID FLOW         KMOL/HR        14.4002
TOP STAGE VAPOR FLOW             KMOL/HR        0.44793
BOILUP VAPOR FLOW                KMOL/HR        27.4163
MOLAR REFLUX RATIO                              1.01929
MOLAR BOILUP RATIO                              1.90388
CONDENSER DUTY (W/O SUBCOOL)     WATT           -297,721.
REBOILER DUTY                    WATT           313,400.
```

| Stream Name	Units	CO2	H2	MIX	MIX-COMP	R-IN	R-OUT	R-OUT-C	SEP-IN	SEP-L	SEP-H	DIST-IN	REC	PURGE	CH3OH-V	CH3OH-L	H2O
Phase		Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase			Vapor Phase	Liquid Phase		Vapor Phase	Vapor Phase	Vapor Phase	Liquid Phase	Liquid Phase
Temperature	C	20	20	32,0733	100	225	255	147,802	35	35	35	64,7	34,9962	34,9962	61,2505	61,2505	94,5681
Pressure	bar	1,01325	1,01325	1,01325	100	100	100	100	100	5	5	1,01325	1,01325	1,01325	1,01325	1,01325	1,01325
Mass Flows	kg/hr	660,147	99,7861	1978,52	1978,52	1978,52	1978,51	1978,51	1978,51	1243,52	734,996	734,996	1218,65	24,8703	15,0213	453,593	266,381
CO2	kg/hr	660,147	0	990,687	990,687	990,687	342,159	342,159	342,159	337,258	4,90096	4,90096	330,513	6,74515	2,90855	1,99241	0,00467871
H2	kg/hr	0	99,7861	626,571	626,571	626,571	537,592	537,592	537,592	537,592	0,120022	0,120022	526,84	10,7518	0,120022	3,3401E-08	1,28662E-46
H2O	kg/hr	0	0	33,5658	33,5658	33,5658	299,037	299,037	299,037	34,2543	264,783	264,783	33,5692	0,685085	0,146183	14,1486	250,488
CO	kg/hr	0	0	44,7189	44,7189	44,7189	45,6919	45,6919	45,6919	45,6302	0,0617306	0,0617306	44,7176	0,912603	0,0588802	0,0028504	4,36756E-16
CH3OH	kg/hr	0	0	282,978	282,978	282,978	754,032	754,032	754,032	288,782	465,251	465,251	283,006	5,77563	11,9076	437,45	15,8929
Mass Fractions																	
CO2		1	0	0,500721	0,500721	0,500721	0,172937	0,172937	0,172937	0,271213	0,006668	0,006668	0,271213	0,271213	0,193629	0,0043925	1,7564E-10
H2		0	1	0,316687	0,316687	0,316687	0,271715	0,271715	0,271715	0,432316	0,0001633	0,0001633	0,432316	0,432316	7,99017E-08	7,36331E-16	4,82999E-49
H2O		0	0	0,0169651	0,0169651	0,0169651	0,151142	0,151142	0,151142	0,0275463	0,360251	0,360251	0,0275463	0,0275463	0,00973176	0,0311922	0,940338
CO		0	0	0,0226022	0,0226022	0,0226022	0,0230941	0,0230941	0,0230941	0,0366945	8,39876E-05	8,39876E-05	0,0366945	0,0366945	0,000391979	6,28404E-06	1,63959E-18
CH3OH		0	0	0,143025	0,143025	0,143025	0,381111	0,381111	0,381111	0,23223	0,632997	0,632997	0,23223	0,23223	0,792719	0,964409	0,0596622
Mole Fractions																	
CO2		1	0	0,0651312	0,0651312	0,0651312	0,0245864	0,0245864	0,0245864	0,0267119	0,00379666	0,00379666	0,0267119	0,0267119	0,147542	0,00312586	7,38257E-11
H2		0	1	0,899306	0,899306	0,899306	0,843343	0,843343	0,843343	0,929567	0,00202987	0,00202987	0,929567	0,929567	1,32919E-06	1,14397E-14	4,43217E-48
H2O		0	0	0,00539086	0,00539086	0,00539086	0,0524929	0,0524929	0,0524929	0,00662775	0,501094	0,501094	0,00662775	0,00662775	0,0181153	0,0542266	0,965556
CO		0	0	0,00461928	0,00461928	0,00461928	0,000515865	0,000515865	0,000515865	0,00567839	7,51365E-05	7,51365E-05	0,00567839	0,00567839	0,00469289	7,02629E-06	1,08281E-18
CH3OH		0	0	0,0255525	0,0255525	0,0255525	0,0744191	0,0744191	0,0744191	0,0314152	0,495034	0,495034	0,0314152	0,0314152	0,829648	0,942641	0,0344439

Table 4 Ideal case simulation results

We were able to set up a PFD according to the theoretical part of the thesis. The simulation in AspenPLUS run successfully, therefore we have a functioning parametric model for this process. This model will be applied in the next chapter and could be applied for any methanol synthesis process simulation.

4. Container technology model in AspenPLUS

With the use of the parametric model in AspenPLUS a container technology of methanol synthesis will be designed in this chapter. The first step will be scaling the parametric model with some potential modifications to the PFD, so that the technology fits into a standard container. Based on that, some basic dimensions of the equipment will be calculated, and a 3D disposition model will be created.

A sketch drawing with dimensions of the container is in Picture 10 below. The container has a door on the front side, a few openings will have to be made for the actual installed container, such as for the piping for the inlet streams, electrical connections and for the ventilation of the working space.
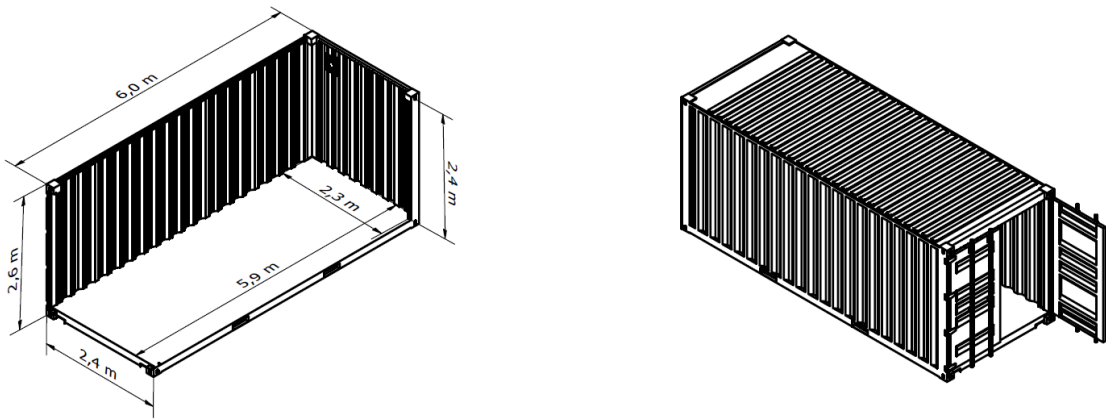
Picture 10 Container sketch

Due to this space requirement the flowrates on the unit entrance had to be downscaled. The final unit inlet flowrates are in Table 5.

H_2	0,57 kg/h
CO_2	3,74 kg/h

Table 5 Inlet flowrates

Unfortunately, some further modifications were needed, because even with the downscaled flowrates, some of the equipment did not fit into the container.

The modified version of the PFD for the container technology is in Picture 11. Two modifications have been done in the general parametric model PFD. The general parametric model is using the heat obtained by the exothermic reaction (stream

R-OUT) to preheat the stream on the reactor inlet. In the container technology simulation, to save some space a less space requiring heater in the form of a heating wire wrapped around the piping was used instead of a heat exchanger.

The second adjustment was done to ensure acceptable dimensions for the separator so that it would fit into the standard 20 feet container. In the general parametric model, a flash separator is used, where the pressure drops to 5 bar. Mainly due to the very low density of hydrogen, which is one of the main separated components, the separator would not fit into the container (calculations were made based on the scriptum of Ditl [26]) when applied to our small-scale plant. In the container technology specific PFD, the pressure is kept at around 100 bar in the separator and the pressure is reduced after the separator. Both methods have been applied in different studies, separation at 100 bar is used in papers of Keshavarz et al. or Luyben et al. The dimension calculations are presented in Chapter 5 below.

Furthermore, in this chapter, verification of the simulation results is done by calculating parts of the simulation (multiple heat exchanges a pressure change, reaction heat for the reactor and distillation column) analytically. All calculations are done only for the container technology simulation results. A slight difference in the results is expected, most of the analytic calculations are done with some simplifying assumptions mentioned in the beginning of this chapter.
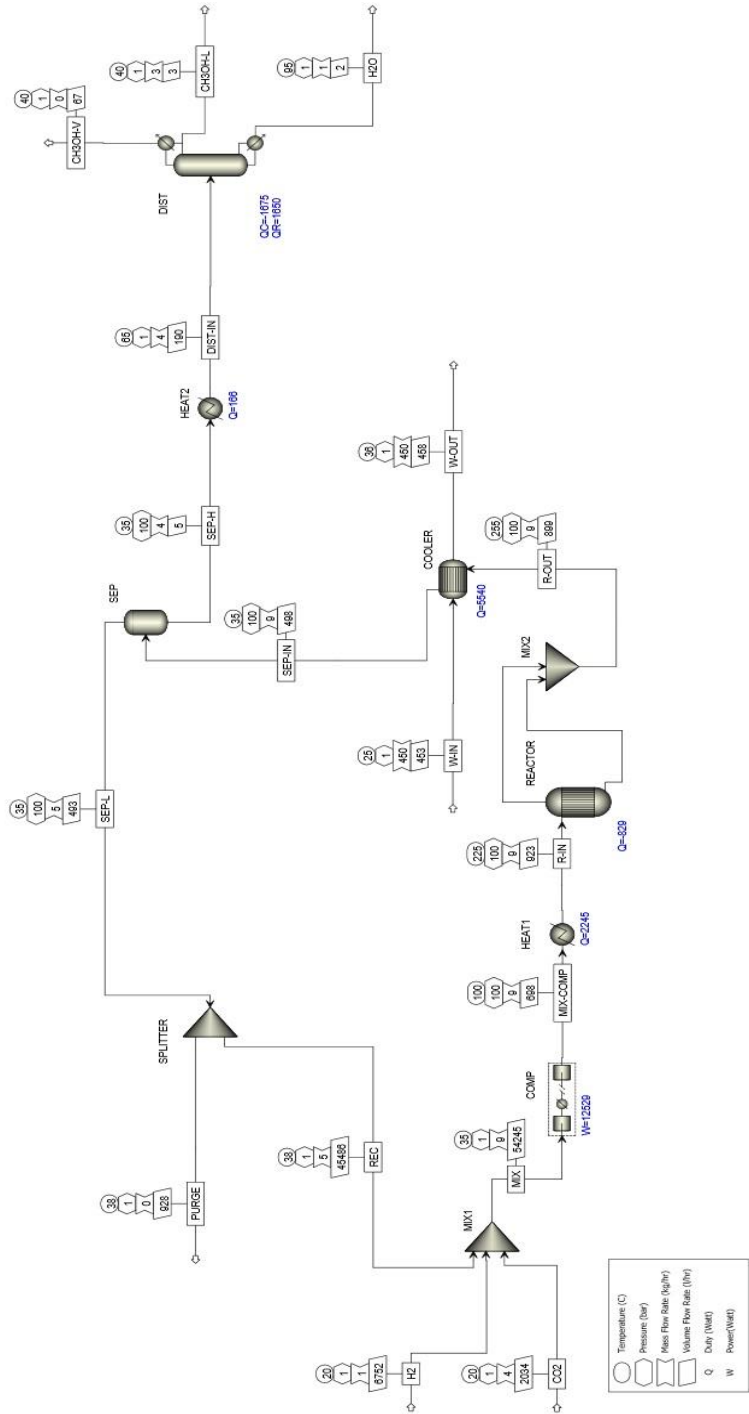
Picture 11 Container technology AspenPLUS flowsheet

The set up for each main apparatus simulation model is presented with the results and the verifying calculation below.

4.1. Compressor

No changes were made to the parametric model compressor setup.

```
BLOCK: COMP    MODEL: MCOMPR
-----------------------------
INLET STREAMS:        MIX              TO STAGE  1
OUTLET STREAMS:       MIX-COMP         FROM STAGE  8

            ***  MASS AND ENERGY BALANCE  ***
                        IN              OUT            RELATIVE DIFF.
TOTAL BALANCE
MOLE(KMOL/HR )          2.14323         2.14323        0.00000
MASS(KG/HR  )           8.80946         8.80946        0.00000
ENTHALPY(WATT  )        -11256.8        -10058.7       -0.106432

            ***  CO2 EQUIVALENT SUMMARY ***
FEED STREAMS CO2E               4.44115    KG/HR
PRODUCT STREAMS CO2E            4.44115    KG/HR
NET STREAMS CO2E PRODUCTION     0.00000    KG/HR
UTILITIES CO2E PRODUCTION       0.00000    KG/HR
TOTAL CO2E PRODUCTION           0.00000    KG/HR

             ***  INPUT DATA  ***
ISENTROPIC CENTRIFUGAL COMPRESSOR
NUMBER OF STAGES               8

             ***  RESULTS  ***
FINAL PRESSURE, BAR            100.000
TOTAL WORK REQUIRED, WATT      12,528.5
TOTAL COOLING DUTY , WATT      -11,330.4
```

4.1.1. Mixture compression calculation

We will calculate the amount of power for the ideal gas and an adiabatic compression. The compression process is divided in 8 stages, after each stage the mixture is cooled down to 100 °C, it is ensured that the temperatures do not exceed 200 °C in any of the stages. The complete calculation below is done for the first two stages. Stages 3-8 are calculated the same way as stage 2.

Compression input data	
p_1	101,325 kPa
p_2	300 kPa
p_3	500 kPa
T_{01}	308,15 K
T_{02}	373,15 K
$\dot{n}_{CO2}$	$2,80313 \cdot 10^{-5}$ kmol/s
$\dot{n}_{H2}$	0,0005647 kmol/s
x_{CO2}	0,0473
x_{H2}	0,953

Table 6 Compression input data

First stage calculation:

$$\kappa = \sum \kappa_i \cdot x_i \tag{7}$$

$$\kappa = (1,4 \cdot 0,953) + (1,33 \cdot 0,0473) = 1,397109 \tag{8}$$

$$T_2 = T_{01} \cdot \left(\frac{p_2}{p_1}\right)^{\frac{\kappa-1}{\kappa}} \tag{9}$$

$$T_2 = 308,15 \cdot \left(\frac{300}{101,325}\right)^{\frac{1,397109-1}{1,397109}} = 419,5 \text{ K} \tag{10}$$

$$W_{t1} = (\dot{n}_{CO2} + \dot{n}_{H2}) \cdot R \cdot T_1 \cdot \frac{\kappa}{\kappa-1} \cdot \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{\kappa-1}{\kappa}}\right] \tag{11}$$

$$W_{t1} = (2,80313 \cdot 10^{-5} + 0,0005647) \cdot 8,314 \cdot 308,15 \cdot \frac{1,397109}{1,397109-1} \cdot \left[1 - \left(\frac{300}{101,325}\right)^{\frac{1,397109-1}{1,397109}}\right] \tag{12}$$

$$W_{t1} = -1,94 \text{ kW} \tag{13}$$

Second stage calculation:

$$T_3 = T_{02} \cdot \left(\frac{p_3}{p_2}\right)^{\frac{\kappa-1}{\kappa}} \tag{14}$$

$$T_3 = 373,15 \cdot \left(\frac{500}{300}\right)^{\frac{1,397109-1}{1,397109}} = 431,5 \text{ K} \tag{15}$$

$$W_{t1} = (\dot{n}_{CO2} + \dot{n}_{H2}) \cdot R \cdot T_2 \cdot \frac{\kappa}{\kappa-1} \cdot \left[1 - \left(\frac{p_3}{p_2}\right)^{\frac{\kappa-1}{\kappa}}\right] \tag{16}$$

$$W_{t1} = (2,80313 \cdot 10^{-5} + 0,0005647) \cdot 8,314 \cdot 373,15 \cdot \frac{1,397109}{1,397109-1} \cdot \left[1 - \left(\frac{500}{300}\right)^{\frac{1,397109-1}{1,397109}}\right] \tag{17}$$

$$W_{t2} = -1,02 \text{ kW} \tag{18}$$

$$W_t = W_{t1} + W_{t2} + W_{t3} + W_{t4} + W_{t5} + W_{t6} + W_{t7} + W_{t8} \tag{19}$$

$$W_t = -1,94 + (-1,02) + (-1,18) + (-0,72) + (-1,24) + (-1,27) + (-1,15) + (-0,43) \tag{20}$$

$$W_t = -8,94 \text{ kW} \tag{21}$$

In Table 7 the results of the simulation and the calculation are compared. As expected, there is an absolute difference, but the number of digits correspond and the difference is justified by the assumptions made in the beginning of this chapter, therefore we can say, that the simulation result is validated.

Calculated quantity	Simulation	Analytic calculation	Absolute difference	Percentage difference
$W_{mixture\ compression}$ [kW]	-12,517	-8,94	3,589	28,65 %

Table 7 Result comparison compression

4.2. Preheater

As was declared before, the heat exchanger that was in this position in the parametric model was replaced with a basic heater, therefore the block model Heater was used. The inlet temperature of the mixture is 100 °C and the outlet temperature is 225 °C. The specified pressure is 100 bar.

```
BLOCK:  HEAT1   MODEL: HEATER
  ------------------------------
INLET STREAM:        MIX-COMP
OUTLET STREAM:       R-IN


        ***  MASS AND ENERGY BALANCE  ***
                       IN              OUT            RELATIVE DIFF.
TOTAL BALANCE
MOLE (KMOL/HR)         2.14323         2.14323        0.00000
MASS (KG/HR)           8.80946         8.80946        0.00000
ENTHALPY (WATT)        -10058.7        -7813.27       -0.223236


        ***  CO2 EQUIVALENT SUMMARY ***
FEED STREAMS CO2E              4.44115    KG/HR
PRODUCT STREAMS CO2E           4.44115    KG/HR
NET STREAMS CO2E PRODUCTION    0.00000    KG/HR
UTILITIES CO2E PRODUCTION      0.00000    KG/HR
TOTAL CO2E PRODUCTION          0.00000    KG/HR


        ***  INPUT DATA  ***
TWO   PHASE  TP  FLASH
SPECIFIED TEMPERATURE      C         225.000
SPECIFIED PRESSURE         BAR       100.000
MAXIMUM NO. ITERATIONS               30
CONVERGENCE TOLERANCE                 0.000100000


        ***  RESULTS  ***
OUTLET TEMPERATURE         C             225.00
OUTLET PRESSURE            BAR           100.00
HEAT DUTY                  WATT          2245.5
OUTLET VAPOR FRACTION                    1.0000
```

4.2.1. Preheating of reactants calculation

Preheating input data	
$n_{mix-comp}$	0,00059534 kmol/s
T_0	373,15 K
T	498,15 K

Table 8 Preheating input data

The composition of the mixture is in Table 9 below.

CO_2	0,047084475
H_2	0,948534755
H_2O	0,000330456
CO	0,002398806
CH_3OH	0,001651508

Table 9 Composition of preheated mixture

First the heat capacity of the mixture is calculated which is then applied in the calorimetric equation to calculate the demanded heat.

	a	b	c	d
CO_2	19,795	0,07344	-6E-05	1,7E-08
H_2	27,143	0,00927	-1E-05	7,6E-09
CH_3OH	21,15	0,07092	3E-05	-3E-08
H_2O	32,243	0,00192	1E-05	-4E-09
CO	30,869	-1,29E-02	2,79E-05	-1,27E-08

Table 10 Heat capacity coefficients

$$c_p = \sum x_i \cdot c_{pi} \tag{22}$$

$$c_{pi} = a + b \cdot T + c \cdot T^2 + d \cdot T^3 \tag{23}$$

$$c_{pCO2} = 19,795 + 0,07344 \cdot 373,15 + -6E\text{-}05 \cdot 373,15^2 +$$
$$+1,7E\text{-}08 \cdot 373,15^3 = 40,282993 \text{ kJ/(kmol·K)} \tag{24}$$

$$c_{pH2} = 29,07789 \text{ kJ/(kmol·K)} \tag{25}$$

$$c_{pCH3OH} = 49,73413 \text{ kJ/(kmol·K)} \tag{26}$$

$$c_{pH2O} = 34,24371 \text{ kJ/(kmol·K)} \quad\quad (27)$$

$$c_{pCO} = 29,29655 \text{ kJ/(kmol·K)} \quad\quad (28)$$

$$c_p = 0,047084475 \cdot 40,282993 + 0,948534755 \cdot 29,07789 + 0,001651508 \cdot 49,73413 +$$
$$+ 0,000330456 \cdot 34,24371 + 0,002398806 \cdot 29,29655 = 29,64125 \text{ kJ/(kmol·K)} \quad (29)$$

$$\dot{Q} = \dot{n} \cdot c_p \cdot \Delta T = 0,00059534 \cdot 29,64125 \cdot (498,15 - 373,15) = 2,206 \text{ kW} \quad (30)$$

In Table 11 the results of the simulation and the calculation are compared. As expected, there is an absolute difference, but the number of digits correspond and the difference is justified by the assumptions made in the beginning of this chapter, therefore we can say, that the simulation result is validated.

Calculated quantity	Simulation	Analytic calculation	Absolute difference	Percentage difference
$Q_{preheating\ of\ reactants}$ [kW]	2,245	2,206	0,039	1,74 %

Table 11 Result comparison preheating

4.3. Reactor

No changes were made to the parametric model reactor setup.

```
BLOCK:  REACTOR  MODEL: REQUIL
  -----------------------------
INLET STREAM:              R-IN
OUTLET VAPOR STREAM:       4
OUTLET LIQUID STREAM:      5


        ***  MASS AND ENERGY BALANCE  ***
                    IN        OUT           GENERATION      RELATIVE DIFF.
TOTAL BALANCE
MOLE (KMOL/HR)      2.14323   1.98021       -0.163018       -0.103603E-15
MASS (KG/HR)        8.80946   8.80946       -0.287626E-09
ENTHALPY (WATT)     -7813.27  -8642.56      0.959540E-01


        ***  CO2 EQUIVALENT SUMMARY ***
FEED STREAMS CO2E            4.44115    KG/HR
PRODUCT STREAMS CO2E         0.845282   KG/HR
NET STREAMS CO2E PRODUCTION  -3.59587   KG/HR
UTILITIES CO2E PRODUCTION    0.00000    KG/HR
TOTAL CO2E PRODUCTION        -3.59587   KG/HR


        ***  INPUT DATA  ***
TWO   PHASE  TP  FLASH
SPECIFIED TEMPERATURE C      255.000
SPECIFIED PRESSURE   BAR     100.000
MAXIMUM NO. ITERATIONS       30
```

```
CONVERGENCE TOLERANCE              0.000100000
SUBSTREAM NO. =   1  MIXED SUBSTREAM, NO SOLID SPLITS.


              ***  RESULTS  ***
OUTPUT TEMPERATURE   C              255.00
OUTPUT PRESSURE     BAR             100.00
HEAT DUTY        WATT               -829.29
VAPOR FRACTION                       1.0000


REACTION EQUILIBRIUM CONSTANTS:


   REACTION        EQUILIBRIUM      EQUILIBRIUM      TEMPERATURE
   NUMBER          CONSTANT         TEMPERATURE      UNIT
     1             0.20833E-04      255.00           C
     2             83.391           255.00           C
```

4.3.1.   Residence time calculation

Since an equilibrium reactor was used, it is not possible to obtain the residence time value from the AspenPLUS simulation. There are two different pathways of obtaining it, both were carried out in this paper.

First is by using process data from different studies. Number of tubes, tube dimensions, porosity, reactor inlet flow rate and the feed composition are required for the calculation. A result overview acquired by this method is in Table 12 below.

Parameter/Study	S. Yusup et al. 2010	L. Chen et al. 2011	A. A. Kiss et al. 2016	Canete et al. 2017	B. Walid et al. 2018	C. Shi et al. 2020	J. Nyáry 2020	W. L. Luyben 2010
Inlet temperature [°C]	225	225	225	230	253	250	230	150
Inlet pressure [bar]	82	69,7	50	71	51	105,65	50	110
Residence time[s]	3,8	3,2	11,4	2,4	2,7	0,9	4,5	9

Table 12 Residence time overview

The second option is to use the catalyst demands given by the GHSV parameter which is usually listed by the manufacturer. In Table 13 below is a list of commercial catalysts fitted for this reaction and the demands given by the manufacturers. In literature the commonly mentioned commercial catalysts were the MK-101 (Haldor-Topsoe) and the ICI KATALCO 51-2. Unfortunately, the accessible data sheets don't contain any valuable technical data for these two catalysts. Only three sets of complete or close to complete catalyst data were found, all three were on the conventional $CuO/ZnO/Al_2O_3$ basis.

Catalyst	MS-2	MegaMax800	RP-60
Manufacturer	Haitai MS-2	Clariant	BASF
Chemical constitution	$CuO/ZnO/Al_2O_3$ based	$CuO/ZnO/Al_2O_3$ based	$CuO/ZnO/Al_2O_3$ based
Dimensions [mm]	ø5x(4.5-5.5)	ø6x(4-5)	ø5x5
Pressure [MPa]	3.0-15.0	2.0-12.5	-
Temperature [°C]	200-300	190-315	200-290
Space velocity [h^{-1}]	7000-20000	25000 $Nm^3/m^3/h$	<10000

Table 13 Catalyst commercial overview

From the space velocity demands we can calculate the residence time. The GHSV (gas hourly space velocity) is defined as the inverse value of residence time, or we can define it with the following formula:

$$GHSV = \frac{\dot{V}}{V_p} \qquad [h^{-1}] \qquad\qquad (31)$$

Where $\dot{V}$ is the volume flow rate and V_p is the volume of the pores.

For our process we set the space velocity at 10000 h^{-1}, all the following calculations were made with the assumption of using the BASF catalyst RP-60 for which this GHSV value is adequate. From this we get a residence time of 0,36 s.

Results obtained from these two methods do not compare, residence time given by the GHSV value is substantially shorter, than those obtained from the process characteristics. The difference will likely be caused by the later. After further exploration, it was found out a common fact amongst the cited studies was that they used part of the input data for their calculations from studies which were studying the process with different process conditions or even a different type of catalyst. This non-compatibility makes the residence times based on these studies unreliable and therefore residence time will be taken according to the GHSV catalyst parameter given by the manufacturers.

4.3.2.   Heat of reaction and reactor power

For this calculation we only take the main chemical reaction (equation 4), into consideration the results will serve just as an approximate verification. The heat produced by the exothermicity of the reaction is calculated for the input data in Table 14 below.

Reactor input data	
T	528,15 K
T_0	298,15 K
n_{CO2in}	$2,8 \cdot 10^{-5}$ kmol/s
n_{CO2out}	$5,3 \cdot 10^{-6}$ kmol/s
X_{CO2}	0,81

Table 14 Input data for reactor calculations

First the reaction heat for the specific operating temperature is calculated.

	φ	a	b	c	d	$\Delta h^{sl}{}_{(g)}$
CO2	-1	19,795	0,07344	-0,00005602	$1,715 \cdot 10^{-8}$	-393,8
H2	-3	27,143	0,009274	-0,00001381	$7,645 \cdot 10^{-9}$	0
CH3OH	1	21,15	0,07092	0,00002587	$-2,852 \cdot 10^{-8}$	-201,3
H2O	1	32,243	0,0019238	0,000010555	$-3,596 \cdot 10^{-9}$	-242

Table 15 Reaction heat coefficients

$$\Delta H_r^T = \Delta H_r^0 + A \cdot (T - T_0) + \frac{1}{2} \cdot B \cdot (T^2 - T_0^2) + \frac{1}{3} \cdot C \cdot (T^3 - T_0^3) + \frac{1}{4} \cdot D \cdot (T^4 - T_0^4) \qquad (32)$$

$$\Delta H_r^0 = \sum \varphi_i \cdot \Delta h_g^{sl} \qquad (33)$$

$$\Delta H_r^0 = (-1) \cdot (-393,8) + (-3) \cdot 0 + 1 \cdot (-201,3) + 1 \cdot (-242) = -49,5 \text{ kJ/mol} \qquad (34)$$

$$A = \sum \varphi_A \cdot a \qquad (35)$$

$$B = \sum \varphi_B \cdot b \qquad (36)$$

$$C = \sum \varphi_C \cdot c \qquad (37)$$

$$D = \sum \varphi_D \cdot d \qquad (38)$$

$$A = (-1) \cdot 19,795 + (-3) \cdot 27,143 + 1 \cdot (21,15) + 1 \cdot (32,243) = -47,831 \qquad (39)$$

$$B = (-1) \cdot 0,07344 + (-3) \cdot 0,009274 + 1 \cdot 0,07092 + 1 \cdot 0,0019238 = -0,0284182 \qquad (40)$$

$$C = (-1) \cdot (-0,00005602) + (-3) \cdot (-0,00001381) + 1 \cdot 0,00002587 + 1 \cdot 0,000010555 =$$
$$= 0,000133875 \qquad (41)$$

$$D = (-1) \cdot 1,715 \cdot 10^{-8} + (-3) \cdot 7,645 \cdot 10^{-9} + 1 \cdot (-2,852 \cdot 10^{-8}) + 1 \cdot (-3,596 \cdot 10^{-9}) =$$
$$= -7,2201 \cdot 10^{-8} \qquad (42)$$

$$\Delta H_r^T = -49,5 + (-47,831) \cdot (528,15 - 298,15) + \frac{1}{2} \cdot (-0,0284182) \cdot (528,15^2 -$$

$$- 298,15^2) + \frac{1}{3} \cdot 0,000133875 \cdot (528,15^3 - 298,15^3) + \frac{1}{4} \cdot -7,2201 \cdot 10^{-8} \cdot (528,15^4 -$$

$$- 298,15^4) = -9621,3 \text{ kJ/mol} \tag{43}$$

From the reaction heat and the degree of completion of the reaction, which is calculated below we calculate the heat that is produced by the chemical reaction.

$$\xi = -\frac{X_{CO2} \cdot n_{CO2in}}{\varphi} = -\frac{0,81 \cdot 2,8 \cdot 10^{-5}}{-1} = -2,268 \cdot 10^{-5} \tag{44}$$

$$\dot{Q}_r = \Delta H_r^T \cdot \xi = -9621,3 \cdot 2,268 \cdot 10^{-5} = 218,2 \text{ W} \tag{45}$$

In Table 16 the results of the simulation and the calculation are compared. As expected, there is an absolute difference, but the number of digits correspond and the difference is justified by the assumptions made in the beginning of this chapter, therefore we can say, that the simulation result is validated.

Calculated quantity	Simulation	Analytic calculation	Absolute difference	Percentage difference
$Q_{reaction\ power}$ [kW]	0,829	0,218	0,611	73,7 %

Table 16 Result comparison reaction power

4.4. Cooler
No changes were made to the parametric model reactor setup.

```
BLOCK:  COOLER   MODEL: HEATX
------------------------------
HOT SIDE:
  ---------
INLET STREAM:              R-OUT
OUTLET STREAM:             SEP-IN
COLD SIDE:
  ----------
INLET STREAM:              W-IN
OUTLET STREAM:             W-OUT
        ***  MASS AND ENERGY BALANCE  ***
                      IN              OUT             RELATIVE DIFF.
TOTAL BALANCE
MOLE (KMOL/HR)        26.9802         26.9802         0.00000
MASS (KG/HR)          459.191         459.191         0.00000
ENTHALPY (WATT)       -0.199337E+07   -0.199337E+07   0.00000


        ***  CO2 EQUIVALENT SUMMARY ***
FEED STREAMS CO2E              0.845282    KG/HR
PRODUCT STREAMS CO2E           0.845282    KG/HR
NET STREAMS CO2E PRODUCTION    0.00000     KG/HR
UTILITIES CO2E PRODUCTION      0.00000     KG/HR
TOTAL CO2E PRODUCTION          0.00000     KG/HR
```

```
FLOW DIRECTION AND SPECIFICATION:
COUNTERCURRENT   HEAT EXCHANGER
SPECIFIED HOT OUTLET TEMP
SPECIFIED VALUE         C                    35.0000
LMTD CORRECTION FACTOR                       1.00000


PRESSURE SPECIFICATION:
HOT  SIDE OUTLET PRESSURE    BAR             100.0000
COLD SIDE PRESSURE DROP      BAR             0.0000


             ***  OVERALL RESULTS  ***
STREAMS:
        -------------------------------------
                    |              |
R-OUT   ----->|         HOT        |-----> SEP-IN
T= 2.5500D+02 |                    |   T= 3.5000D+01
P= 1.0000D+02 |                    |   P= 1.0000D+02
V= 1.0000D+00 |                    |   V= 9.1607D-01
                    |              |
W-OUT   <-----|         COLD       |<----- W-IN
T= 3.5722D+01 |                    |   T= 2.5000D+01
P= 1.0132D+00 |                    |   P= 1.0132D+00
V= 0.0000D+00 |                    |   V= 0.0000D+00
        -------------------------------------
DUTY:
CALCULATED HEAT DUTY      WATT         5539.6954
```

4.4.1.   Cooler calculation

Products of the chemical reaction are cooled with water as the cooling medium in a heat exchanger, only the cold side will be calculated.

Cooler input data	
$n_{mix\text{-}comp}$	0,0069445 kmol/s
T_0	298,15 K
T	308,87 K
c_{pmix}	74,1 kJ/(kmol·K)

Table 17 Cooling of reaction products input data

$$Q= \dot{n} \cdot c_p \cdot \Delta T = 0{,}0069445 \cdot 74{,}1 \cdot (308{,}87 - 298{,}15) = 5{,}15 \text{ kW} \quad (46)$$

In Table 18 the results of the simulation and the calculation are compared. As expected, there is an absolute difference, but the number of digits correspond and the difference is justified by the assumptions made in the beginning of this chapter, therefore we can say, that the simulation result is validated.

Calculated quantity	Simulation	Analytic calculation	Absolute difference	Percentage difference
$Q_{\text{cooling of reaction products}}$ [kW]	5,540	5,15	0,39	7,04 %

Table 18 Result comparison cooling reaction products

4.5. Separator

The same simulation block is used for the separator as is in the parametric model, but with a slightly different setting. The pressure is set to 100 bar instead of 5 bar.

```
 BLOCK:  SEP    MODEL: FLASH2
 ------------------------------
INLET STREAM:                   SEP-IN
OUTLET VAPOR STREAM:            SEP-L
OUTLET LIQUID STREAM:           SEP-H
```

```
         ***  MASS AND ENERGY BALANCE  ***
                        IN              OUT             RELATIVE DIFF.
TOTAL BALANCE
MOLE (KMOL/HR)          1.98021         1.98021         0.00000
MASS (KG/HR)            8.80946         8.80946         0.00000
ENTHALPY (WATT)         -14182.3        -14182.3        0.339987E-11
```

```
         ***  CO2 EQUIVALENT SUMMARY ***
FEED STREAMS CO2E               0.845282   KG/HR
PRODUCT STREAMS CO2E            0.845282   KG/HR
NET STREAMS CO2E PRODUCTION     0.00000    KG/HR
UTILITIES CO2E PRODUCTION       0.00000    KG/HR
TOTAL CO2E PRODUCTION           0.00000    KG/HR
```

```
           ***  INPUT DATA  ***
TWO   PHASE  TP  FLASH
SPECIFIED TEMPERATURE C         35.0000
SPECIFIED PRESSURE   BAR        100.000
MAXIMUM NO. ITERATIONS          30
CONVERGENCE TOLERANCE           0.000100000
```

```
           ***  RESULTS  ***
OUTLET TEMPERATURE   C          35.000
OUTLET PRESSURE      BAR        100.00
HEAT DUTY            WATT        -0.76842E-12
VAPOR FRACTION                  0.91607
```

4.6. Heater

No changes were made to the parametric model reactor setup.

```
BLOCK:  HEAT2   MODEL: HEATER
 ------------------------------
INLET STREAM:       SEP-H
OUTLET STREAM:      DIST-IN
```

```
         ***  MASS AND ENERGY BALANCE  ***
                        IN              OUT             RELATIVE DIFF.
```

```
TOTAL BALANCE
MOLE (KMOL/HR)              0.166190        0.166190        0.00000
MASS (KG/HR)               4.21438         4.21438          0.00000
ENTHALPY (WATT)           -12193.3        -12027.0         -0.136368E-01


        *** CO2 EQUIVALENT SUMMARY ***
FEED STREAMS CO2E              0.130691    KG/HR
PRODUCT STREAMS CO2E          0.130691    KG/HR
NET STREAMS CO2E PRODUCTION    0.00000    KG/HR
UTILITIES CO2E PRODUCTION      0.00000    KG/HR
TOTAL CO2E PRODUCTION          0.00000    KG/HR


        *** INPUT DATA ***
TWO   PHASE  TP  FLASH
SPECIFIED TEMPERATURE      C              64.7000
SPECIFIED PRESSURE         BAR            1.01325
MAXIMUM NO. ITERATIONS                    30
CONVERGENCE TOLERANCE                     0.000100000


        *** RESULTS ***
OUTLET TEMPERATURE         C              64.700
OUTLET PRESSURE            BAR            1.0132
HEAT DUTY                  WATT           166.28
OUTLET VAPOR FRACTION                     0.40545E-01
```

4.6.1.   Heating of distillation column inlet

The heavy fraction of from the separator is heated before entering the distillation column. The same procedure is used for this calculation as for the preheating of reactants.

$n_{mix\text{-}comp}$	$4,61639 \cdot 10^{-5}$ kmol/s
T_0	308,15 K
T	338,55 K
c_{pmix}	75,7 kJ/(kmol·K)

Table 19 Distillation column input data

$$Q = \dot{n} \cdot c_p \cdot \Delta T = 4,61639 \cdot 10^{-5} \cdot 75,7 \cdot (338,55 - 308,15) = 0,10624 \text{ kW} \qquad (47)$$

In Table 20 the results of the simulation and the calculation are compared. As expected, there is an absolute difference, but the number of digits correspond and the difference is justified by the assumptions made in the beginning of this chapter, therefore we can say, that the simulation result is validated.

Calculated quantity	Simulation	Analytic calculation	Absolute difference	Percentage difference
$Q_{heating\ of\ DC\ inlet}$ [kW]	0,116	0,10624	0,013	11,52 %

Table 20 Result comparison heating of DC inlet

4.7. Distillation column

The same simulation block is used for the distillation column as is in the parametric model, but with a slightly different setting. The distillate rate had to be scaled down.

```
BLOCK: DIST    MODEL: RADFRAC
-------------------------------
INLETS:            DIST-IN          STAGE  5
OUTLETS:           CH3OH-V          STAGE  1
                   CH3OH-L          STAGE  1
                   H2O              STAGE  9
```

*** MASS AND ENERGY BALANCE ***

	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE (KMOL/HR)	0.166190	0.166190	-0.167011E-15
MASS (KG/HR)	4.21438	4.21438	-0.266455E-08
ENTHALPY (WATT)	-12027.0	-12051.6	0.204032E-02

*** CO2 EQUIVALENT SUMMARY ***

FEED STREAMS CO2E	0.130691	KG/HR
PRODUCT STREAMS CO2E	0.130691	KG/HR
NET STREAMS CO2E PRODUCTION	0.381624E-07	KG/HR
UTILITIES CO2E PRODUCTION	0.00000	KG/HR
TOTAL CO2E PRODUCTION	0.381624E-07	KG/HR

**** INPUT PARAMETERS ****

NUMBER OF STAGES	9
ALGORITHM OPTION	STANDARD
ABSORBER OPTION	NO
INITIALIZATION OPTION	STANDARD
HYDRAULIC PARAMETER CALCULATIONS	NO
INSIDE LOOP CONVERGENCE METHOD	BROYDEN
DESIGN SPECIFICATION METHOD	NESTED
MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS	25
MAXIMUM NO. OF INSIDE LOOP ITERATIONS	10
MAXIMUM NUMBER OF FLASH ITERATIONS	30
FLASH TOLERANCE	0.000100000
OUTSIDE LOOP CONVERGENCE TOLERANCE	0.000100000

**** COL-SPECS ****

MOLAR VAPOR DIST / TOTAL DIST	0.030000
MOLAR REFLUX RATIO	0.86499
MOLAR DISTILLATE RATE KMOL/HR	0.086871

*** SUMMARY OF KEY RESULTS ***

TOP STAGE TEMPERATURE	C	40.2883
BOTTOM STAGE TEMPERATURE	C	94.7592
TOP STAGE LIQUID FLOW	KMOL/HR	0.075142
BOTTOM STAGE LIQUID FLOW	KMOL/HR	0.079319
TOP STAGE VAPOR FLOW	KMOL/HR	0.0026061
BOILUP VAPOR FLOW	KMOL/HR	0.14429
MOLAR REFLUX RATIO		0.86499

MOLAR BOILUP RATIO		1.81910
CONDENSER DUTY (W/O SUBCOOL)	WATT	-1,674.80
REBOILER DUTY	WATT	1,650.20

4.7.1.   Distillation column calculation

The basic calculations for the distillation column were next to the simulation done also using the graphical McCabe-Thiele method. The whole calculation will not be presented here, the results were similar, and the number of treys and the inlet trey were the same as in the simulation results.

Table 21 Container technology simulation results

Stream Name	Units	H2	CO2	MIX	MIX-COMP	R-IN	R-OUT	SEP-IN	SEP-H	SEP-L	DIST-IN	REC	PURGE	CH3OH-L	CH3OH-V	H2O
Phase		Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase		Liquid Phase	Vapor Phase		Vapor Phase	Vapor Phase	Liquid Phase	Vapor Phase	Liquid Phase
Temperature	C	20	20	35,1338	100	225	255	35	35	35	64,7	38,4898	38,4898	40,2883	40,2883	94,7592
Pressure	bar	1,01325	1,01325	1,01325	100	100	100	100	100	100	1,01325	1,01325	1,01325	1,01325	1,01325	1,01325
Mass Flows	kg/hr	0,565454	3,74083	8,80946	8,80946	8,80946	8,80946	8,80946	4,21438	4,59509	4,21438	4,50318	0,0919018	2,64616	0,102534	1,46568
CO2	kg/hr	0	3,74083	4,44115	4,44115	4,44115	0,845282	0,845282	0,130691	0,714592	0,130691	0,700316	0,0142918	0,058532	0,0721587	5,0594E-05
H2	kg/hr	0,565454		4,09813	4,09813	4,09813	3,6048	3,6048	0,0119609	3,6048	0,0119609	3,53268	0,072096	1,8142E-09	0,0119609	8,6397E-48
H2O	kg/hr	0	0	0,0127592	0,0127592	0,0127592	1,48472	1,48472	1,4717	0,01302	1,4717	0,0127592	0,000260399	0,0895754	0,000314752	1,38181
CO	kg/hr	0	0	0,144007	0,144007	0,144007	0,149526	0,149526	0,00258227	0,146944	0,00258227	0,144007	0,000293888	0,000170247	0,00241202	7,5428E-14
CH3OH	kg/hr	0	0	0,113415	0,113415	0,113415	2,72514	2,72514	2,60941	0,115733	2,60941	0,113415	0,00231466	2,49789	0,0276482	0,0838719
Mass Fractions																
CO2		0	1	0,504134	0,504134	0,504134	0,0959516	0,0959516	0,0310107	0,155512	0,0310107	0,155516	0,155512	0,0221196	0,703755	3,4519E-05
H2		1	0	0,465197	0,465197	0,465197	0,409196	0,409196	0,00283812	0,78449	0,00283812	0,784486	0,78449	6,8559E-10	0,116653	5,8947E-49
H2O		0	0	0,000144835	0,000144835	0,000144835	0,168537	0,168537	0,349209	0,00283345	0,349209	0,00283338	0,00283345	0,033851	0,00366974	0,942776
CO		0	0	0,0163468	0,0163468	0,0163468	0,0169734	0,0169734	0,000612728	0,0319785	0,000612728	0,0319789	0,0319785	6,43373	0,0235241	5,1463E-14
CH3OH		0	0	0,0128742	0,0128742	0,0128742	0,309342	0,309342	0,619168	0,0251863	0,619168	0,0251856	0,0251863	0,943965	0,26965	0,0572239
Mole Fractions																
CO2		0	1	0,0470845	0,0470845	0,0470845	0,00969932	0,00969932	0,0178686	0,0089509	0,0178686	0,00895117	0,0089509	0,0157834	0,629137	1,4493E-05
H2		1	0	0,948535	0,948535	0,948535	0,903037	0,903037	0,0357022	0,985768	0,0357022	0,985767	0,985768	1,068E-10	0,22767	5,4033E-47
H2O		0	0	0,000330456	0,000330456	0,000330456	0,041619	0,041619	0,491555	0,000398407	0,491555	0,000398398	0,000398407	0,059007	0,006704	0,967
CO		0	0	0,000239881	0,000239881	0,000239881	0,0026958	0,0026958	0,000554723	0,000289195	0,000554723	0,002892	0,000289195	7,21299	0,0330421	3,3949E-14
CH3OH		0	0	0,00165151	0,00165151	0,00165151	0,0429493	0,0429493	0,490021	0,00199111	0,490021	0,00199106	0,00199111	0,925138	0,331094	0,0330001

We were able to set up a container technology specific PFD based on the parametric model. The simulation in AspenPLUS run successfully, therefore we have a functioning model specifically for scale of the process. Some of the simulated variables were verified with an analytic calculation. The results of this model will be used in the next chapter for the dimension calculations.

5. Container technology design and layout

In this chapter first some of the demands for the technology layout will be discussed, after that, basic dimensions for the main equipment will be calculated and a 3D disposition model will be created.

5.1. Working space ergonomics

To ensure the ergonomics within the plant, some guidelines need to be followed when designing the layout of the container.

Considering that the only access of light is through the front door and only when it is opened, some sufficient additional illumination will be needed and even more so in case of the plant running continuously.

The next issue to keep in mind is to have sufficient ventilation in place.

In regards to the layout of the plant, the anthropometry measurements that are shown in Picture 12 below were taken into consideration, so that the worker has enough space to safely operate the unit.
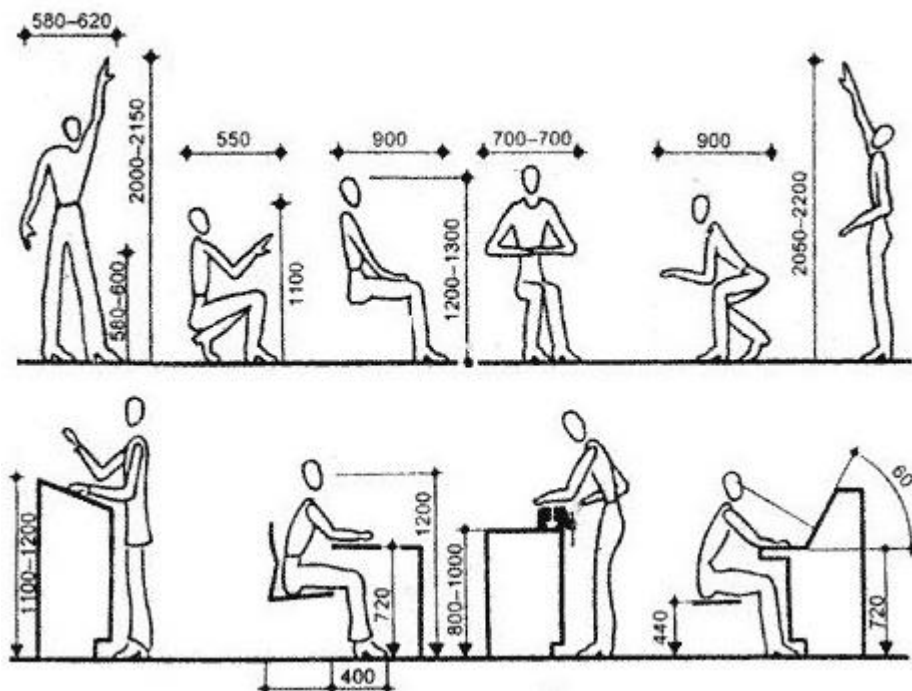
Picture 12 Anthropometry for plant ergonomics [21]

The process is automated and therefore other than the exchange of the product filling bottles, some maintenance and occasional operational or service actions should not occur.

5.2. Design calculations

Only the fundamental dimensions were calculated for each of the three main apparatuses.

5.2.1. Reactor design

As was already established, the residence time will be calculated according to the demands of the catalyst. The basis for the calculation will be the GHSV criteria given by the manufacturer.

volume flow of reactor inlet	15,38498 l/min
GHSV	10000 h^{-1}
porosity	0,4

Table 22 Reactor design input

$$\dot{V} = 15,38498 \text{ l/min} = 0,923099 \text{ m}^3/h = 0,0003 \text{ m}^3/s \tag{48}$$

$$V_p = \frac{\dot{V}}{GHSV} = \frac{0,923099}{10000} = 9,23 \cdot 10^{-5} \text{ m}^3 \tag{49}$$

$$\tau = \frac{V_p}{\dot{V}} = \frac{9,23 \cdot 10^{-5}}{0,0003} = 0,36 \text{ s} \tag{50}$$

$$V_{total} = \frac{V_p}{\varepsilon} = \frac{9,23 \cdot 10^{-5}}{0,4} = 0,000231 \text{ m}^3 = 230774,7 \text{ mm}^3 \tag{51}$$

Chosen tube length	200 mm
Chosen tube inner diameter	10 mm
Chosen tube outer diameter	14 mm

Table 23 Chosen tube parameters

$$S = \pi \cdot \left(\frac{D}{2}\right)^2 = \pi \cdot \left(\frac{10}{2}\right)^2 = 78,54 \text{ mm}^2 \tag{52}$$

$$V_{tube} = S \cdot L = 78,54 \cdot 200 = 15707,96 \text{ mm}^3 \tag{53}$$

$$n_T = \frac{V_{total}}{V_{tube}} = \frac{230774,7}{15707,96} = 14,69 \text{ tubes} \tag{54}$$

$$n_T = 15 \text{ tubes} \tag{55}$$

$$t = 1,3 \cdot d_e = 1,3 \cdot 14 = 18,2 \tag{56}$$

$$D_{min} = 2 \cdot t \cdot \sqrt{\frac{n_T}{\pi \cdot 1,15}} = 2 \cdot 18,2 \cdot \sqrt{\frac{15}{\pi \cdot 1,15}} = 74,17 \text{ mm} \tag{57}$$

$$D_{real} = 100 \text{ mm} \tag{58}$$

Further calculation results

Reactor wall thickness	8 mm
Tube sheet thickness	9 mm

Table 24 Reactor design results

5.2.2. Separator design

The separator is equipped with a demister. The separator calculations were done according to the scriptum of Ditl [26].

L	0,166189 kmol/h
V	1,805679 kmol/h
ρ_V	9,175268 kg/m³
ρ_L	843,2352 kg/m³
Mv	2,539127 kg/mol

Table 25 Separator input data

K_{drum} is an empiric constant and Blackwell (1984) suggest an empiric expression as follows for a separator with a demister as follows:

$$K_{drum}=0,29\ exp\left[A+B\cdot ln\ F_{lv}+C\cdot(ln\ F_{lv})^2+D\cdot(ln\ F_{lv})^3+E\cdot(ln\ F_{lv})^4\right] \quad (59)$$

A	-1,87748
B	-0,81458
C	-0,18707
D	-0,01452
E	-0,00101

Table 26 Blackwell constants

$$F_{lv}=\frac{L}{V}\cdot\sqrt{\frac{\rho_V}{\rho_L}}=\frac{0,166189}{1,805679}\cdot\sqrt{\frac{9,175268}{843,2352}}=0,0096 \quad (60)$$

$K_{drum} = 0,29\ exp\left[-1,87748 + (-0,81458)\cdot ln\ 0,0096 + (-0,18707)\right.$

$\left.\cdot(ln\ 0,0096)^2 + (-0,01452)\cdot(ln\ 0,0096)^3 + (-0,00101)\cdot(ln\ 0,0096)^4\right] = 0,0923 \quad (61)$

$$u_{perm} = K_{drum}\cdot\sqrt{\frac{\rho_L-\rho_V}{\rho_V}}=0,0923\cdot\sqrt{\frac{843,2352-9,175268}{9,175268}}=0,88\ m/s \quad (62)$$

$$S_{drum}=\frac{V\cdot M_V}{3600\cdot u_{perm}\cdot\rho_V}=\frac{1805,679\cdot 2,539127}{3600\cdot 0,88\cdot 9,175268}=0,158\ m^2 \quad (63)$$

$$D=\sqrt{\frac{4\cdot S_{drum}}{\pi}}=\sqrt{\frac{4\cdot 0,158}{\pi}}=0,448246\ m \quad (64)$$

The recommended ratio between the diameter and the horizontal length of the vessel is between 3 − 5.

$$L_{hor}= 3 \cdot D = 3 \cdot 0{,}448246 = 1{,}344739 \text{ m} \tag{65}$$

$$D_{real}=0{,}5 \text{ m} \tag{66}$$

$$L_{real}=1{,}5 \text{ m} \tag{67}$$

5.2.3.   Distillation column design

The design calculations for the distillation column are done according to Hands, Whitt.

$$\dot{n}=D \cdot \left(1+R_{opt}\right)= 0{,}084 \cdot (1+0{,}891)=0{,}159 \tfrac{\text{kmol}}{\text{h}} = 4{,}428 \cdot 10^{-5} \text{ kmol/s} \tag{68}$$

$$\dot{V}_g= \frac{\dot{n} \cdot R \cdot T}{p} = \frac{4{,}428 \cdot 10^{-5} \cdot 8{,}314 \cdot 338{,}65}{101{,}325} = 0{,}0012295 \text{ m}^3/\text{s} \tag{69}$$

$$S_k= \frac{\dot{V}_g}{u} = \frac{0{,}0012295}{0{,}2} = 0{,}0061476 \text{ m}^2 \tag{70}$$

$$d= \sqrt{\frac{4 \cdot S_k}{\pi}} = \sqrt{\frac{4 \cdot 0{,}0061476}{\pi}} = 0{,}08847 \text{ m} \tag{71}$$

Enriching section

$\dot{m}_L$	0,000458 kg/s
μ_L	0,3965 mPas
d	0,08847 m
d_0	0,0015 m

Table 27 Enriching section input data

$$\phi_L= \frac{4 \cdot \dot{m}_L}{\pi \cdot d^2} = \frac{4 \cdot \dot{m}_L}{\pi \cdot d^2} = \frac{4 \cdot 0{,}000458}{\pi \cdot 0{,}08847^2} = 0{,}07455 \text{ kg/(m·s)} \tag{72}$$

$$HETP_e= 70 \cdot \left(\frac{d_0 \cdot \mu_L}{\phi_L}\right) = 70 \cdot \left(\frac{0{,}0015 \cdot 0{,}3965}{0{,}07455}\right) = 0{,}1977 \text{ m} \tag{73}$$

Stripping section

$\dot{m}_L$	0,00175 kg/s
μ_L	0,369 mPas
d	0,08847 m
d_0	0,0015 m

Table 28 Stripping section input data

$$\phi_L= \frac{4 \cdot \dot{m}_L}{\pi \cdot d^2} = \frac{4 \cdot \dot{m}_L}{\pi \cdot d^2} = \frac{4 \cdot 0{,}00175}{\pi \cdot 0{,}08847^2} = 0{,}2845 \text{ kg/(m·s)} \tag{74}$$

$$HETP_s= 70 \cdot \left(\frac{d_0 \cdot \mu_L}{\phi_L}\right) = 70 \cdot \left(\frac{0{,}0015 \cdot 0{,}3965}{0{,}2845}\right) = 0{,}07973 \text{ m} \tag{75}$$

$$H = 5 \cdot HETP_s+4 \cdot HETP_e= 5 \cdot 0{,}1977+4 \cdot 0{,}07973=1{,}1098 \text{ m} \tag{76}$$
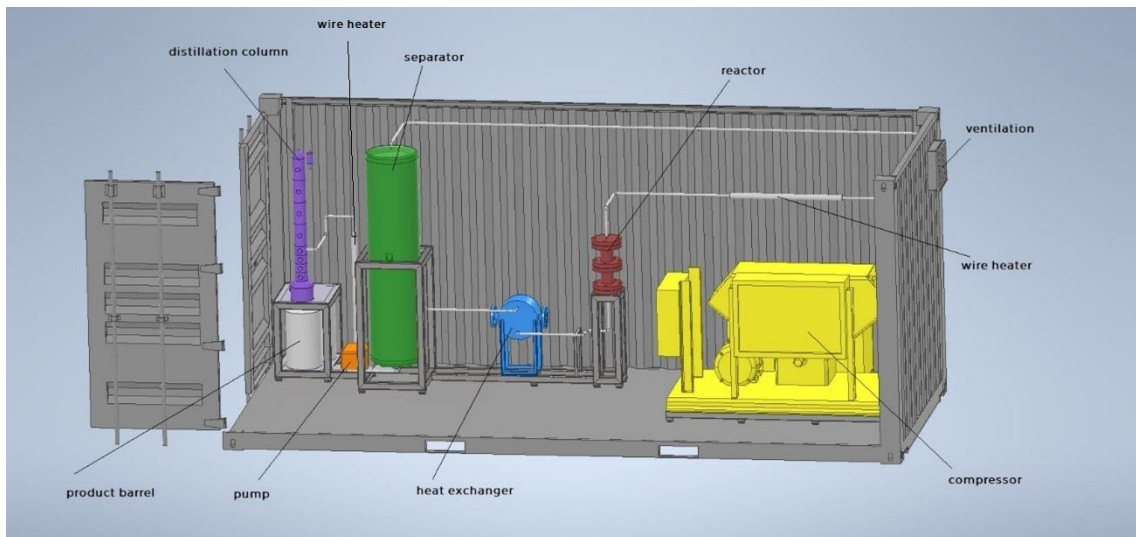
5.3. Container layout

Based on the design calculations and the anthropometry measurements a 3D layout was made as well as a 2D drawing. The layout does not include all the components that would have to be in place at a functioning plant, and some components are just symbolised rather than being designed such as the HMI or the ventilation. This layout should solely serve the purpose of demonstrating and determining whether this technology can fit into the standard 20 feet container. A more detailed layout was therefore not necessary.
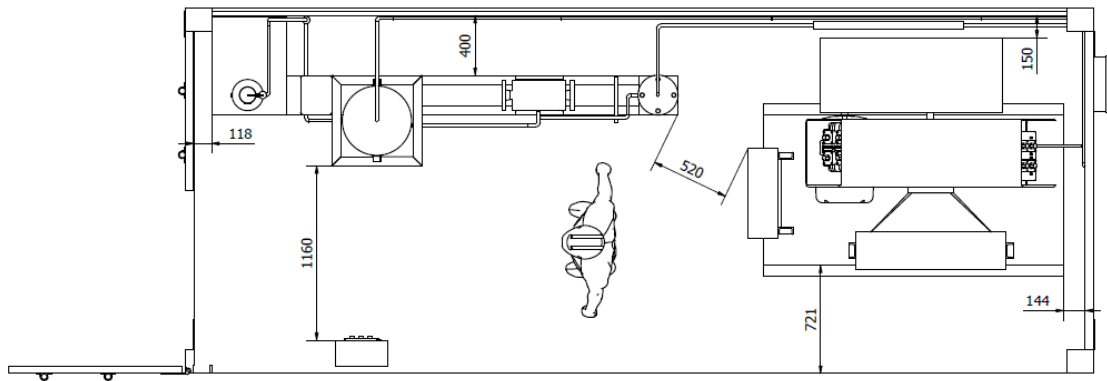
Picture 13 Container technology layout drawing

The 3D model is in the Picture 14 below, all the equipment is labelled.

Picture 14 3D container technology layout

5.4.   Specification sheets

Below all the proposed mechanical equipment as well as all the instrumentation and fittings are listed with specified process conditions, control system and if possible, some specifications from available options on the market.

5.4.1.   Compressor specification sheet

Due to its size the compressor is one of the key components for the overall layout of the unit. An oilless piston compressor was chosen because of the character of the compressed chemicals. The compressor is electrically powered. A possible configuration with moisture separators given by the manufacturer would preferably be applied.

Picture 15 RIX Industries 4VX [24]

Compressor RIX Industries 4VX – G-110	
Apparatus specifications	
Technology	Piston compressor
	Oil-free
	4 stages
	Moisture separator included
Inlet Pressure	Ambient
Outlet Pressure	Up to 410 bar
Volume Flow Range	0.85-5.66 m^3/min
Motor	18.65 kW
Control system	
Flow sensor	PE-111
Pressure sensor	FE-112
Process Conditions	
Inlet medium	mixture of CO_2 and H_2, with minority content of H_2O, CO, CH_3OH
Volume flow	0,904086 m^3/min
Inlet pressure	1,01325 bar
Outlet pressure	100 bar
Inlet temperature	35 °C
Outlet temperature	100

5.4.2. Reactor specification sheet

A variation of Lurgi's isothermal tube reactor was chosen for this application. The reactor is water cooled. Since this would be a pilot unit, an option to use different catalysts would be advantageous. A change in residence time would be in some cases necessary and therefore as is shown in Picture 14 it would be possible to change the needed residence time prolonging the reactor by connecting two reactors in series with a flange connection. The catalyst is usually in form of either pellets as is the case with our preferred BASF catalyst RP-60 (1,5x1,5 mm) or tablets (ø5x5 mm). The catalyst will need to be grinded into smaller pieces which is a common practice with small scale units.

Reactor – R-210	
Apparatus specifications	
Technology	Isothermic reactor
	Tube reactor
Material	Stainless steel DIN 1.4571
Catalyst	$Cu\text{-}ZnO\text{-}Al_2O_3$
Control system	
Temperature sensor	TE-211
Temperature sensor	TE-212
Pressure sensor	PE-215
Process conditions	
Inlet medium	mixture of CO_2 and H_2, with minority content of H_2O, CO, CH_3OH
Operating pressure	100 bar
Operating temperature	255 °C

5.4.3.   Separator specification sheet

The separator is a basic pressure vessel with a built-in demister. The material was chosen based on the character of the chemicals. The vessel is also equipped with lug supports.

Separator – D-310	
Apparatus specifications	
Technology	Phase separator
	Built in demister
Material	Stainless steel DIN 1.4571
Control system	
Level sensor	LE-311-1
Level sensor	LE-311-2
Pressure sensor	PE-312
Temperature sensor	TE-316
Temperature sensor	TE-317
Process conditions	
Inlet medium	Mixture of H_2, CH_3OH and H_2O with minority content of CO, CO_2
Operating pressure	100 bar
Operating temperature	35 °C

5.4.4. Heater specification sheet

Surface heating with a heating cable with mineral insulation is applied in two locations, first as a preheater for the reactants, that enter the reactor and the second serves as a distillation column preheater.

Picture 16 Heating cable with mineral insulation [25]

Heater – E-211	
Apparatus specifications	
Technology	Heating cable wrap
	Mineral insulation
Material	AISI 516
Process conditions	
Heated medium inlet	mixture of CO_2 and H_2, with minor content of H_2O, CO, CH_3OH
Heated medium inlet pressure	100 bar
Heated medium inlet temperature	100 °C
Heating power	2,245 kW

Heater – E-411	
Apparatus specifications	
Technology	Heating cable wrap
	Mineral insulation
Material	AISI 516
Process conditions	
Heated medium inlet	mixture of CH_3OH and H_2O, with minor content of H_2, CO, CO_2
Heated medium inlet pressure	1,01325 bar
Heated medium inlet temperature	35 °C
Heating power	0,116 kW

5.4.5.   Heat exchanger specification sheet

A shell and plate heat exchanger was chosen to cool the reaction products with water as the coolant.

Picture 17 Heat exchanger

Shell and plate cooler Gesmex XPS50 – E-213	
Apparatus specifications	
Technology	Single pass
	Cross flow
Material	AISI 516
Coolant	Water
Process conditions	
Hot side inlet medium	Mixture of H_2, CH_3OH and H_2O with minority content of CO, CO_2
Hot side inlet pressure	100 bar
Hot side inlet temperature	255 °C
Hot side outlet pressure	100 bar
Hot side outlet temperature	35 °C

5.4.6. Pump peristaltic

Peristaltic pump Verdflex Vantage 5000 Modbus	
Apparatus specifications	
Technology	Peristaltic
Process conditions	
Inlet medium	Mixture of CH_3OH and H_2O with minority content of H_2, CO and CO_2
Operating inlet pressure	1,01325 bar
Operating inlet temperature	35 °C
Operating flowrate	3,16681 l/min

5.4.7. Distillation column specification sheet

Distillation column – D-410	
Apparatus specifications	
Technology	Plate column with condenser
	9 treys
	Inlet on 5th trey
Process conditions	
Cold side inlet medium	mixture of CH_3OH and H_2O, with minor content of H_2, CO, CO_2
Inlet pressure	1,01325 bar
Inlet temperature	64,7 °C

5.4.8. Instrumentation

Below is an overview of the proposed instrumentation. The measured quantities were flowrate, pressure, temperature, level and chemical composition.

Pressure sensor PE-111
Purpose: indication and control, placed on the outlet of compressor (G-110), connected to compressor (G-110)
Medium: mixture of CO_2 and H_2, with minor content of H_2O, CO, CH_3OH
Operating temperature: 100°C
Operating pressure: 100 bar
Temperature range: -40 °C − 125 °C
Pressure range: 0 - 600 bar
Accuracy: max. ±1,5 % FS

Flow sensor FE-112
Purpose: indication and control, placed on the outlet of compressor (G-110), connected to flow control valve (FCV-112)
Medium: mixture of CO_2 and H_2, with minor content of H_2O, CO, CH_3OH
Operating temperature: 100°C
Operating pressure: 100 bar
Mass flow: 8,80946 kg/h
Flow range: 3 - 22 l/min
Temperature range: 0 °C − 100 °C
Pressure range: 0 - 300 bar

Temperature sensor TE-211
Purpose: indication and control, placed on the reactor (R-210), connected to heater (E-211)
Medium: mixture of H_2, CO_2, H_2O, CO and CH_3OH
Operating temperature: 255°C
Operating pressure: 100 bar
Temperature range: -50 °C - 400 °C

Temperature sensor TE-212
Purpose: indication and control, placed on the reactor (R-210), connected to flow control valve of cooling water
Medium: mixture of H_2, CO_2, H_2O, CO and CH_3OH
Operating temperature: 255°C
Operating pressure: 100 bar
Temperature range: -50 °C - 400 °C

Temperature sensor TE-213
Purpose: indication and control, placed on outlet of the heat exchanger (E-213), connected to flow control valve (FCV-213)
Medium: mixture of CH_3OH and H_2O, with minor content of H_2, CO, CO_2
Operating temperature: 35 °C
Operating pressure: 100 bar
Temperature range: -50 °C - 400 °C

Pressure sensor PE-215
Purpose: indication and control, placed on the reactor (R-210), connected to flow control valve (PCV-215)
Medium: mixture of H_2, CO_2, H_2O, CO and CH_3OH
Operating temperature: 255 °C
Operating pressure: 100 bar
Mass flow: 8,80946 kg/h
Temperature range: 125 °C - 1200 °C
Pressure range: 20 - 6000 bar

Level sensor LE-311-1
Purpose: indication and control, placed on the separator (D-310), connected to pump (P-320)
Medium: mixture of H_2, CH_3OH and H_2O with minority content of CO and CO_2
Operating temperature: 35 °C
Operating pressure: 100 bar
Mass flow: 8,80946 kg/h
Temperature range: -20 °C - 85 °C
Pressure range: 0 - 200 bar
Accuracy: ±0,75% FS

Level sensor LE-311-2
Purpose: indication and control, placed on the separator (D-310), connected to pump (P-320)
Medium: mixture of H_2, CH_3OH and H_2O with minority content of CO and CO_2
Operating temperature: 35°C
Operating pressure: 100 bar
Mass flow: 8,80946 kg/h
Temperature range: -20 °C - 85 °C
Pressure range: 0 - 200 bar
Accuracy: ±0,75% FS

Pressure sensor PE-312
Purpose: indication, placed on the separator (D-310)
Medium: mixture of H_2, CH_3OH and H_2O with minority content of CO and CO_2
Operating temperature: 35°C
Operating pressure: 100 bar
Mass flow: 4,59509 kg/h
Temperature range: -40 °C - 125°C
Pressure range: 0 - 600 bar
Accuracy: max. ±1,5 % FS

Temperature sensor TE-316
Purpose: indication, placed on the separator (D-310)
Medium: mixture of H_2, CO_2, H_2O, CO and CH_3OH
Operating temperature: 35 °C
Operating pressure: 100 bar
Temperature range: -50 °C - 400 °C

Temperature sensor TE-317
Purpose: indication, placed on the separator (D-310)
Medium: mixture of H_2, CO_2, H_2O, CO and CH_3OH
Operating temperature: 35 °C
Operating pressure: 100 bar
Temperature range: -50 °C - 400 °C

Temperature sensor TE-411
Purpose: indication and control, placed on the outlet of the heater E-411, connected to heater E-411
Medium: mixture of CH_3OH, H_2O, H_2, CO_2, CO_2 and CO
Operating temperature: 64,7 °C
Operating pressure: 1,01325 bar
Mass flow: 4,21438 kg/h
Temperature range: -50 °C - 400 °C

Flow sensor FE-412
Purpose: indication and control, placed on the outlet of distillation column (D-410), connected to flow control valve (FCV-412)
Medium: mixture of CH_3OH, H_2O, H_2, CO_2, CO_2 and CO
Operating temperature: 40,3 °C
Operating pressure: 1,01325 bar
Volume flow: 0,0563627 l/min
Flow range: 0,0005 – 0,5 l/min
Pressure range: 0 - 145 bar
Accuracy: max. ±0,8 % FS

Flow sensor FE-413
Purpose: indication and control, placed on the outlet of distillation column (D-410), connected to flow control valve (FCV-413)
Medium: mixture of CH_3OH, H_2O, H_2, CO_2, CO_2 and CO
Operating temperature: 40,3 °C
Operating pressure: 1,01325 bar
Volume flow: 0,102534 l/min
Flow range: 0,4 − 1,8 l/min
Temperature range: 0 °C − 100 °C
Pressure range: 0 - 250 bar

Flow sensor FE-414
Purpose: indication and control, placed on the outlet of distillation column (D-410), connected to flow control valve (FCV-414)
Medium: mixture of CH_3OH, H_2O, H_2, CO_2, CO_2 and CO
Operating temperature: 100°C
Operating pressure: 100 bar
Volume flow: 0,0269196 l/min
Flow range: 0,0005 − 0,5 l/min
Pressure range: 0 - 145 bar
Accuracy: max. ±0,8 % FS

5.4.9. Fittings

Below is an overview of the proposed fittings. Most of the fittings were flow regulating valves, check valves, draining valves and pressure regulation valves were proposed as well.

Flow control valve FCV-112
Purpose: Regulation of flow, placed on the outlet of the compressor (G-110), connected to sensor FE-112
Medium: mixture of CO_2 and H_2, with minor content of H_2O, CO, CH_3OH
Operating temperature: 100°C
Operating pressure: 100 bar
Temperature range: -20 °C − 350 °C
Pressure range: 0 − 160 bar

Check valve V-113
Purpose: Ensures one way flow, placed after the inlet of H_2
Medium: H_2
Operating temperature: 20 °C
Operating pressure: 1,01325 bar
Temperature range: -20 °C − 70 °C
Pressure range: 0-25 bar

Check valve V-114
Purpose: Ensures one way flow, placed after the inlet of CO_2
Medium: CO_2
Operating temperature: 20°C
Operating pressure: 1,01325 bar
Temperature range: -20 °C − 70 °C
Pressure range: 0-25 bar

Flow control valve FCV-115
Purpose: Regulation of flow, placed after the inlet of H_2, connected to sensor AE-115
Medium: H_2
Operating temperature: 20°C
Operating pressure: 1,01325 bar
Volume flow: 112,525 l/min
Temperature range: -10 °C – 60 °C
Pressure range: up to 10 bar
Volume flow range: 0 – 185 l/min

Flow control valve FCV-116
Purpose: Regulation of flow, placed after the inlet of CO_2, connected to sensor AE-116
Medium: CO_2
Operating temperature: 20°C
Operating pressure: 1,01325 bar
Volume flow: 33,8997 l/min
Temperature range: -10 °C – 70 °C
Pressure range: up to 100 bar
Volume flow range: 0 – 50 l/min

Flow control valve TCV-213
Purpose: Regulation of flow, placed on the heat exchanger cold side inlet (E-213), connected to sensor TE-213
Medium: H_2O
Operating temperature: 25 °C
Operating pressure: 1,01325 bar
Volume flow: 7,552 l/min
Temperature range: -10 °C – 70 °C
Pressure range: up to 100 bar
Volume flow range: 0 – 50 l/min

Drain valve V-214
Purpose: Draining outlet, placed on the reactor (R-210) outlet
Medium: mixture of CO_2 and H_2, with minor content of H_2O, CO, CH_3OH
Operating temperature: 255 °C
Operating pressure: 100 bar
Temperature range: -17°C - 260 °C
Pressure range: 0 - 1034 bar

Flow control valve PCV-215
Purpose: Regulation of flow, placed on the outlet of the reactor (R-210), connected to sensor PE-215
Medium: mixture of CO_2 and H_2, with minor content of H_2O, CO, CH_3OH
Operating temperature: 255 °C
Operating pressure: 100 bar
Temperature range: -20 °C – 350 °C
Pressure range: 0 – 160 bar

Pressure regulation valve K-313
Purpose: Regulation of pressure, placed on the outlet of the separator (D-310)
Medium: mixture of H_2, CO_2, H_2O, CO and CH_3OH
Operating temperature: 35 °C
Operating pressure: 100 bar
Temperature range: - 40 °C - 75 °C
Pressure range: 0 - 250 bar

Pressure regulation valve K-314
Purpose: Regulation of pressure, placed on the outlet of the separator (D-310)
Medium: mixture of CH_3OH and H_2O with minor content of H_2, CO and CO_2
Operating temperature: 35 °C
Operating pressure: 100 bar
Temperature range: - 40 °C - 75 °C
Pressure range: 0 - 250 bar

Drain valve V-315
Purpose: Draining outlet, placed on the separator (D-310) outlet
Medium: mixture of H_2, CO_2, H_2O, CO and CH_3OH
Operating temperature: 35 °C
Operating pressure: 100 bar
Temperature range: -40 °C - 121 °C
Pressure range: 0 - 414 bar

Flow control valve PCV-412
Purpose: Regulation of flow, placed on the outlet of distillation column (D-410), connected to sensor FE-412
Medium: mixture of CH_3OH, CO_2, H_2, H_2O, CO
Operating temperature: 40,3 °C
Operating pressure: 1,01325 bar
Volume flow: 0,0563627 l/min
Temperature range: -20 °C - 100 °C
Pressure range: 0 – 210 bar
Volume flow range: 0 – 20 l/min

Flow control valve PCV-413
Purpose: Regulation of flow, placed on the outlet of distillation column (D-410), connected to sensor FE-413
Medium: mixture of CH_3OH, CO_2, H_2, H_2O, CO
Operating temperature: 40,3 °C
Operating pressure: 1,01325 bar
Volume flow: 1,10889 l/min
Temperature range: -20 °C - 100 °C
Pressure range: 0 − 210 bar
Volume flow range: 0 − 20 l/min

Flow control valve PCV-414
Purpose: Regulation of flow, placed on the outlet of distillation column (D-410), connected to sensor FE-414
Medium: mixture of CO_2 and H_2, with minor content of H_2O, CO, CH_3OH
Operating temperature: 94,8 °C
Operating pressure: 1,01325 bar
Volume flow: 0,0269196 l/min
Temperature range: -20 °C - 100 °C
Pressure range: 0 − 210 bar
Volume flow range: 0 − 20 l/min

6. Container technology economical analysis

In this section we will analyse the investment cost and the feasibility of this small-scale technology. To abide the low emission technology concept, we will take green energy into account as well as green resources of material.

6.1. Operating costs of energetic and material resources (OPEX)

First the price for the input chemicals is determined. The price for hydrogen is taken for the green hydrogen alternative.

Chemical	Price of 1 kg	Mass flow kg/h	Total price per hour
H_2	5,50 €	0,57	3,14 €
CO_2	0,12 €	3,74	0,45 €

Table 29 Chemical cost

Catalyst manufacturers usually don't state the prices in catalogues. Only one price range was found for the catalyst MS-2 of the Chinese manufacturer Haitai on an online auction server. The price range is 16 - 70 €. For our calculations we will take the price as 45 €.

The next thing that we have to consider is the catalyst lifetime. Unfortunately, no manufacturer states this information publicly. The exact value is dependent on each process independently and for that reason it is very hard to estimate it. We will calculate with the catalyst lifetime value of 1000 h. One more thing that needs to be estimated is the density of the catalyst, for our calculation we will use the value of 700 kg/m^3. From the porosity and the volume of the reactor determined in the reactor design section we can calculate the weight of one reactor filling.

Catalyst	Price of 1 kg	Price per one filling	Catalyst lifetime [h]	Total price per hour
Cu-ZnO-Al$_2$O$_3$	45,00 €	4,37 €	1000	0,004 €

Table 30 Catalyst cost

The next table summarises the energy demands of the plant. The price of electricity used for this calculation is 0,184 €/kWh.

Apparatus	Energy demand [kW]	Cost of apparatus energy demand [€/h]
Compressor	18,65	3,43
Heater	2,245	0,41
Reactor	0,829	0,15
Cooler	5,54	1,02
Heater	0,116	0,021
Pump	0,23	0,04
Distillation column condenser	1,675	0,31
Distillation column boiler	1,65	0,30
total		5,69 €/h

Table 31 Apparatus energy cost

There are two things with which we can make some profit with this process. First is selling the produced methanol and the second is applying for the EUA funding, which is done by the European Union as part of the climate change policy.

Chemical	Price of 1 kg	Mass flow kg/h	Total amount per hour
CH_3OH	0,34 €	2,7	0,91 €

Table 32 Methanol price

Funding	Price of 1 ton	CO_2 mass flow kg/h	Total amount per hour
EUA	53,00 €	3,74	0,20 €

Table 33 EUA funding

The total operating cost is calculated as the sum of all the previous costs.

Resource	Total hourly operational cost
Material cost	-3,59 €/h
Energy cost	-5,69 €/h
Material profit	0,91 €/h
EUA profit	0,20 €/h
total	-8,17 €/h

Table 34 Total cost

The calculated operational cost is high, and unfortunately it would not be feasible. If we would use brown hydrogen (with the price at 1,68 €), the total hourly operational cost would drop down to -5,99 €/h.

The EU funding is not a big factor at this moment. The price of the EUA is likely going to increase in the following years, it is expected to increase to up to 90 €/t of CO_2 by the year 2030. [22] This increase would however not have a big impact on the total hourly operational cost, since it would only increase the funded amount per hour from 0,2 to 0,34 €/h and the total hourly operational cost would in that case be -5,85 €/h.

6.2. Capital cost of technology (CAPEX)

To calculate the capital cost for this project we will use the Factorial Method by Hand et al. publicised by Towler et al. First an estimation of the cost for the major equipment items is made. After that we calculate the total capital cost using a set of factors.

The price of major equipment items will preferably be taken according to the manufacturer - in Table 35 as [1]. If the manufacturers price is not available or if it is specially fabricated an estimated price will be used instead, using either the website matche.com – in Table 35 as [2], which has an available cost estimation script. In some cases, the price is calculated using the formula from the publication of Towler et al., in Table 35 as [3].

Apparatus	Marking	Price	Source
Reactor	R-210	15 881,00 €	[2]
Compressor	G-110	22 387,00 €	[2]
Separator	D-310	8 110,00 €	[2]
Heater	E-211	380,00 €	[1]
Heater	E-411	20,00 €	[1]
Heat exchanger	E-213	7 856,00 €	[2]
Distillation column	D-410	5 331,50 €	[2,3]
total		59 965,50 €	

Table 35 Apparatus cost

In Table 36 below are all the applied factors and their chosen values. The reserve for material price fluctuation factor was chosen based on that it is a relatively small project. The design factor value was chosen based on the fact that it is a relatively new technology.

f_n	Construction investment, instrumentation, piping, fittings	40%
f_r	Reserve for material price fluctuation	10%
f_d	Design factor	20%

Table 36 CAPEX factors

$$C_n = f_n \cdot C = 0,4 \cdot 59\,965,50 = 23\,986,20 \ € \qquad (77)$$

$$C_r = f_r \cdot C = 0,1 \cdot 59\,965,50 = 5\,996,55 \ € \qquad (78)$$

$$C_d = f_d \cdot C = 0,2 \cdot 59\,965,50 = 11\,993,10 \ € \qquad (79)$$

$$C_{total} = C + C_n + C_r + C_d = 59965,5 + 35979,3 + 5996,55 + 11993,1 = 101\,941,35 \ € \qquad (80)$$

The total capital cost of technology estimation for the methanol conversion container technology is 101 943,35 €.

7. Conclusions

The topic of conversion of CO_2 to methanol is current which was proven by the amount of available literature. However, the technology is still in early stages of improving the methods that were taken over from the conventional syngas synthesis or developing new methods. A lot of the literature is focused on developing a novel catalyst suited specifically for this chemical reaction and a lot of simulations are available as well. Where the research is lacking is the transition into practice, experimental data and specific applications and design of the process.

In the theoretical part of this thesis, the key parameters of the conversion of CO_2 to methanol, such as the conditions of the chemical reaction, the PFD, the catalyst, and basic reactor design were researched and the basis for our parametric model was determined based on this research.

In the practical part of this thesis the key parameters of the process were declared based on the research – the chemical reaction conditions of 255 °C, 100 bar and the H_2 to CO_2 molar ratio of 1:3,3, a Lurgi type reactor was chosen as well as the conventional $Cu\text{-}ZnO\text{-}Al_2O_3$ catalyst and a basic block diagram was created. A parametric simulation model was then created in AspenPLUS based on this data and the PFD, the results and all the settings for each block model were presented.

This model was then applied for designing a container technology scale version of this process. The parametric model had to be scaled down and two modifications to the PFD were needed. The data from the simulation was verified by analytic calculations. Next the basic dimensions for the main apparatuses were calculated based on the data from the simulation and a 3D model and a 2D drawing were created to verify if the technology can fit into a standard 20 feet container. Specification sheets for the proposed apparatuses, sensors and fittings were presented. The designed process then underwent an economical analysis that included operating and capital cost calculations.

It was proven that it was possible to implement the technology into a standard 20 feet container, however the input streams had to be scaled down to 3,74 kg/h CO_2 and 0,57 kg/h of H_2. This shows, that even for a small-scale implementation, the space demands of the technology are substantial mainly due to the size of the compressor and the separator. The designed unit produces 2,5 kg/h of liquid methanol.

The economic analysis shows, that the technology is not feasible on the designed scale. The currently considered parameter that could possibly change that is the

EUA funding, which is expected to go up in the coming years, but even with the expected rise in funding, the technology would not be feasible. Therefore, the fundings would have to go up more drastically than expected. It is likely that this is the main reason why this technology didn't transition from theory into practice on a larger scale.

Whilst this technology is applicable from the technological standpoint and has potential from the environmental standpoint, from the financial standpoint it does not make sense in the current circumstances.

Citations

1. Carbon dioxide [online]. Wikipedia [vid. 20. 3. 2020]. Available at: https://en.wikipedia.org/wiki/Carbon__dioxide

2. Methanol [online]. Wikipedia [vid. 20. 3. 2020]. Available at: https://en.wikipedia.org/wiki/Methanol

3. Synthesis gas [online]. Wikipedia [vid. 20. 3. 2020]. Available at: https://en.wikipedia.org/wiki/Syngas

4. Hydrogen [online]. Wikipedia [vid. 20. 3. 2020]. Available at: https://en.wikipedia.org/wiki/Hydrogen

5. BOWKER, Michael. Methanol sythesis from CO_2 hydrogenation. Chemcatchem minireviews [online]. November 2019, pp. 4238-4246. [vid. 20.3.2020]. ISSN 0005-1098. Available at doi: 10.1002/cctc.201900401

6. GUIL-LÓPEZ, R., N. MOTA, J. LLORENTE, E. MILLÁN, B. PAWELEC, J.L.G. FIERRO and R. M. NAVARRO. Methanol Synthesis from CO_2: A Review of the Latest Developments in Heterogeneous Catalysis. MDPI journal [online]. November 2019, pp. 3902. [vid. 20.3.2020]. Available at doi: 10.3390/ma12233902

7. KAR, Sayan, Jotheeswari KOTHANDARAMAN, Alain GOEPPERT, G.K. Surya PRAKASH. Advances in catalytic homogeneous hydrogenation of carbon dioxide to methanol. Journal of CO_2 utilization [online]. 2018, pp. 212-218. [vid. 20.3.2020]. Available at doi: https://doi.org/10.1016/j.jcou.2017.10.023

8. SCHARNAGL, Florian Korbinian, Maximilian Franz HERTRICH, Gordon NEITZEL, Ralf JACKSTELL, Matthias BELLERA. Homogeneous Catalytic Hydrogenation of CO_2 to Methanol –Improvements with Tailored Ligands. Advanced Sythesis and Catalysis [online]. December 2018, pp. 374-379. [vid. 20.3.2020]. Available at doi: https://doi.org/10.1002/adsc.201801314

9. WANG, Wei, Shengping WANG, Xinbin MA and Jinlong GONG. Recent Advances in Catalytic Hydrogenation of Carbon Dioxide. Chemical Society Reviews [online]. July 2011, pp. 3369-4260. [vid. 20.3.2020]. Available at doi: 10.1039/c1cs15008a

10. WESSELBAUM, Sebastian, Verena MOHA, Markus MEURESCH, Sandra BROSINSKI, Katharina M. THENERT, Jens KOTHE, Thorsten VOM STEIN, Ulli ENGLERT, Markus HÖLSCHER, Jürgen KLANKERMAYER and Walter LEITNER. Hydrogenation of carbon dioxide to methanol using a homogeneous ruthenium – Triphos catalyst: from mechanistic investigations to

multiphase catalysis. The royal society of chemistry [online]. 2015, pp. 693-704 [vid. 24.3.2020]. Available at doi: 10.1039/c4sc02087a

11. ZHONG, Jiawei, Xiaofeng YANG, Zhilian WU, Binglian LIANG, Yanqiang HUANG and Tao ZHANG. State of the art and perspectives in heterogeneous catalysis of CO2 hydrogenation to methanol. Chemical society reviews [online]. 2020, pp. 1325-1616 [vid. 30.3.2020]. Available at doi: 10.1039/c9cs00614a

12. PÉREZ-FORTES, Mar, Jan C. SCHÖNEBERGER, Aikaterini BOULAMANTI, Evangelos TZIMAS. Methanol synthesis using captured CO2 as raw material: Techno-economic and environmental assessment. Applied energy [online]. 2015, pp. 718-733 [vid. 3.4.2020]. Available at doi: 10.1016/j.apenergy.2015.07.067

13. GONZÁLEZ-GARAY, Andrés, Matthias S. FREI, Amjad AL-QAHTANI, Cecilia MONDELLI, Gonzalo GUILLÉN-GOSÁLBEZ and Javier PÉREZ-RAMÍREZ. Plant-to-planet analysis of CO_2-based methanol processes. Royal society of chemistry [online]. 2019, pp. 3425-3436 [vid. 30.3.2020]. Available at doi: 10.1039/c9ee01673b

14. NIEMINEN, Harri, Arto LAARI and Tuomas KOIRANEN. CO2 Hydrogenation to Methanol by a Liquid-Phase Process with Alcoholic Solvents: A Techno-Economic Analysis. Processes [online]. 2019, 405 (7) [vid. 30.3.2020]. Available at doi: 10.3390/pr7070405

15. KISS, Anton A., J. J. PRAGT, H. J. Vos, G. BARGEMAN, M. T. de GROOT. Novel efficient process for methanol synthesis by CO_2 hydrogenation. Chemical Engineering Journal [online]. 2016, pp. 260-269 [vid. 30.3.2020]. Available at doi: 10.1016/j.cej.2015.08.101

16. MATZEN, Michael, Mahdi ALHAJJI, and Yaşar DEMIREL. Chemical storage of wind energy by renewable methanol production: Feasibility analysis using a multi-criteria decision matrix. Energy [online]. 2015, 93, pp. 343-353 [vid. 30.3.2020]. Available at doi: 10.1016/j.energy.2015.09.043

17. ROODE-GUTZMER, Quirina I., Doreen KAISER, Martin BERTAU. Renewable Methanol Synthesis. ChemBioEng Reviews [online]. December 2019, 6, pp. 209-236 [vid. 2.8.2021]. Available at doi: 10.1002/cben.201900012

18. MARLIN, Dana S., Emeric SARRON, Ómar SIGURBJÖRNSSON. Process Advantages of Direct CO_2 to Methanol Synthesis. Front. Chem [online]. September 2018, 6, pp. 446 [vid. 2.8.2021]. Available at doi: 10.3389/fchem.2018.00446

19. ÁLVAREZ, Andrea, Atul BANSODE, Atsushi URAKAWA, Anastasiya V. BAVYKINA, Tim A. WEZEDONK, Michiel MAKKEE, Jorge GASCON, Freek KAPTEIJN. Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO_2 Hydrogenation Processes. Chem. Rev. [online]. July 2017, 117(14), pp. 9804-9838 [vid. 2.8.2021]. Available at doi: 10.1021/acs.chemrev.6b00816

20. Reactors [online]. JUST ChE course material [vid. 2. 8. 2021]. Available at: https://www.just.edu.jo/~yahussain/files/reactors.pdf

21. History and Basics of Anthropometry [online]. Gharpedia [vid. 3. 8. 2021]. Available at: https://gharpedia.com/blog/history-and-basics-of-anthropometry/

22. EU carbon price hits record 50 euros per tonne on route to climate change [online]. Reuters [vid. 3. 8. 2021]. Available at: https://www.reuters.com/business/energy/eu-carbon-price-tops-50-euros-first-time-2021-05-04/

23. ZHEN, Xudong, Yang WANG. An overview of methanol as an internal combustion engine fuel. Renewable and Sustainable Energy Reviews [online]. July 2015. 52. pp. 477-493 [vid. 4. 8. 2021]. Available at doi: 10.1016/j.rser.2015.07.083

24. Nitrogen compression RIX Industries 4VX [online]. NDVA [vid. 5. 8. 2021]. Available at: http://www.ndva.ru/oborudovanie/gaz/4vx_kompressor_gazoviy.html

25. Surface cable heating with mineral insulation [online]. Henlich [vid. 5. 8. 2021]. Available at: https://meres.hennlich.cz/produkty/povrchove-ohrevy-topne-kabely-s-mineralni-izolaci-180/topny-kabel-s-mineralni-izolaci-serie-imi-kmv.html

26. DITL, Pavel. Difúzně separační pochody. Vyd. 3. Praha ČVUT, 2008. ISBN 978-80-01-03972-4.

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