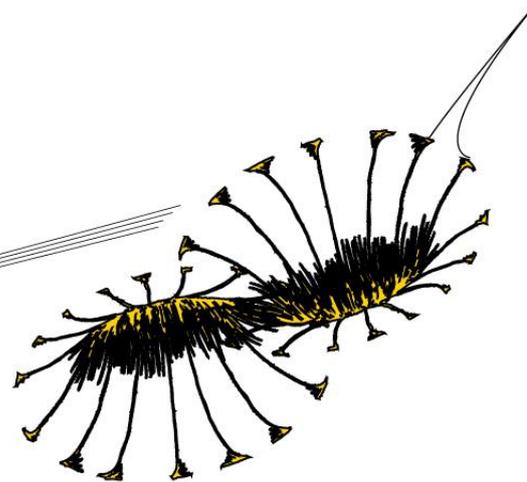




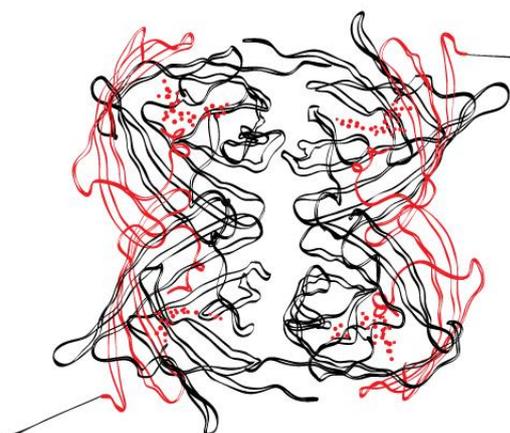
# The production of dimethyl carbonate from methanol and CO<sub>2</sub>

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## Abstract

This research deals with the production of dimethyl carbonate (DMC) through a reaction between methanol and CO<sub>2</sub>. The reaction also produces water and has an equilibrium on the side of the reactants, this leads to a maximum single pass conversion of 1%. Thus a dehydrating agent (2-cyanopyridine) is used to increase the conversion. The plant is designed to be able to supply DMC as an anti knocking agent to a large refinery, the plant capacity is 450 kton DMC per annum, with a purity of 99.8 wt%.

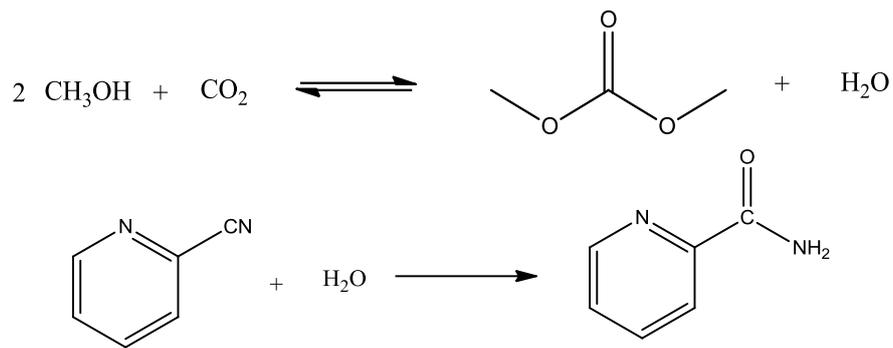


Figure 1: The main reactions in the system

The process was designed in a systematic manner, starting with a conceptual phase, followed by assigning unit operations to separation blocks. A UNISIM simulation was used to make and quantify decisions. In addition, the simulation was used to optimize the process. All the major equipment were designed, which include a variety of reactors, distillation columns, flash vessels, compressors, heaters, coolers, pumps.

The methanol and CO<sub>2</sub> react to DMC in the reactor with a conversion of 92.4%. The unreacted species are separated from the stream and recycled back to the reactor in multiple steps. The reacted dehydrating agent is regenerated and recycled with the unreacted agent to the reactor. The CO<sub>2</sub> is recycled with little pressure drop and the dehydrating agent is separated by distillation. Finally, the methanol/DMC azeotrope is broken by using extractive distillation with phenol as a solvent.

A lot is unknown about regenerating the reacted agent. Therefore this part of the process is not considered. The investment cost are \$33 million and the process is estimated to yield a profit of \$57 million per year. Regeneration section not included. A sensitivity analysis was made to estimate the impact of the regeneration section. A maximum loss of 1.4% of the 2-cyanopyridine is allowable. Significant investment is possible in the regeneration section, while remaining profitable. To conclude; regeneration needs further investigation.

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## Introduction

The interest in sustainable and 'green' process routes is increasing. Depletion of fossil fuels results in increasing CO<sub>2</sub> emissions. The increasing CO<sub>2</sub> level in the atmosphere is linked to unwanted climate change [1]. Governments try to regulate CO<sub>2</sub> emissions with penalties. As a result the number of capture facilities is rapidly increasing.[2]

Thus CO<sub>2</sub> availability is increasing. The next step is not to store the CO<sub>2</sub>, but to convert it into valuable chemicals. The direct conversion of CO<sub>2</sub> with methanol into dimethyl carbonate (DMC) is an example of this. DMC has potential as an anti knocking agent and can possibly (partially) replace MTBE and/or ethanol as a fuel additive.[3] In addition, DMC can potentially replace dimethyl sulfate and methyl halides in methylation reactions [4]. It may also be suitable to replace phosgene as a carbonylation agent for the production of polycarbonates and urethane polymers [4]. DMC is relatively non toxic, especially in comparison to the mentioned chemicals[5].

The main challenge is to overcome the low direct conversion of methanol and CO<sub>2</sub> to DMC, about ~1% [6]. Recently an interesting paper was published by Bansode et al. They showed a very high single pass conversion and selectivity for the direct conversion with the use of a dehydrating agent [7]. However, the recovery of this agent is not elaborated. Strategies to increase the single pass conversion are evaluated in this report and the use of a dehydrating agent is examined further.

In this report a systematic manner is used to develop a industrial scale process from the lab scale experiments. The very first stage consist of a black box evaluation. Thereafter conceptual designs are made. These are turned into unit operations in a systematic way by evaluating all the suitable options. When the final process flow diagram is made, the level of detail is increased until a good first economic estimation can be made. At the end an evaluation is made, whether this process can become a viable industrial production plant.

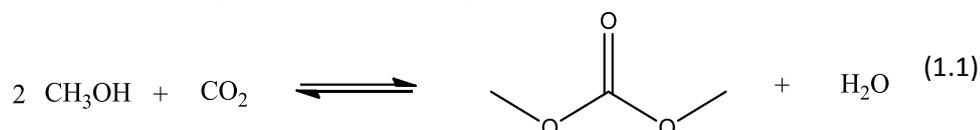
## 1 Scope and design basis



Dimethyl carbonate (DMC) is a relatively new chemical on the market. Although it has been known for longer times, only until recently the use was limited to two main usages. DMC is mainly used as an organic solvent in synthesis of other compounds and as a monomer of polycarbonates (51% of the world production is used for this purpose) [3]. However, only till a few years ago the potential usages were not seen. DMC could be used as a basis for organic paints due to its low boiling point (90°C) and ability to dissolve a wide range of compounds. The main interest for this research is the possibility to use DMC as an anti-knocking agent due to the high oxygen content in the molecule [3, 8].

Currently, other molecules are added for anti-knocking purposes, like ethanol and methyl tert-butyl ether (MTBE). However, these molecules contain less oxygen. Higher oxygen value generally leads to higher octane numbers, higher flexibility in temperature usage and lower carbon monoxide in the flue gasses. The octane number of DMC is comparable to the ones of ethanol and MTBE: 105 for DMC, 113 for ethanol and 95 for MTBE, respectively [9-11].

Various production methods for DMC have been used in the past but recently a more 'green' production method was developed as is shown in equation (1.1) [12].



The equilibrium conditions for this reaction are very much in favour of the methanol and carbon dioxide (CO<sub>2</sub>) [7]. Reached conversions are in the range of 1-2% [13]. To be able to reach sufficient conversion, the reaction conditions will have to be altered.

The goal of the project is for the DMC production to be competitive with the ethanol and MTBE production for anti-knocking purposes. A large refinery which uses DMC as its main fuel additive will need about 10 000 barrels per day, this comes down to 450 kton per year [14]. This is a very large amount compared to the world production. Nevertheless, when it is used instead of another fuel additive it will not saturate the world market, because it opens up a new market for DMC [3]. The DMC will be mixed in with the diesel at about 10-20 w/w% [15]. This leads to higher fuel caloric values and lower smoke/CO emissions, but higher slightly NO<sub>x</sub> emissions [15].

The aim is to design a production process that is sustainable, within reasonable means. The goal for the purity will initially be 99.8% purity as is the standard now for use as a solvent or in synthesis [16]. The design specifications are summarized in Table 1.

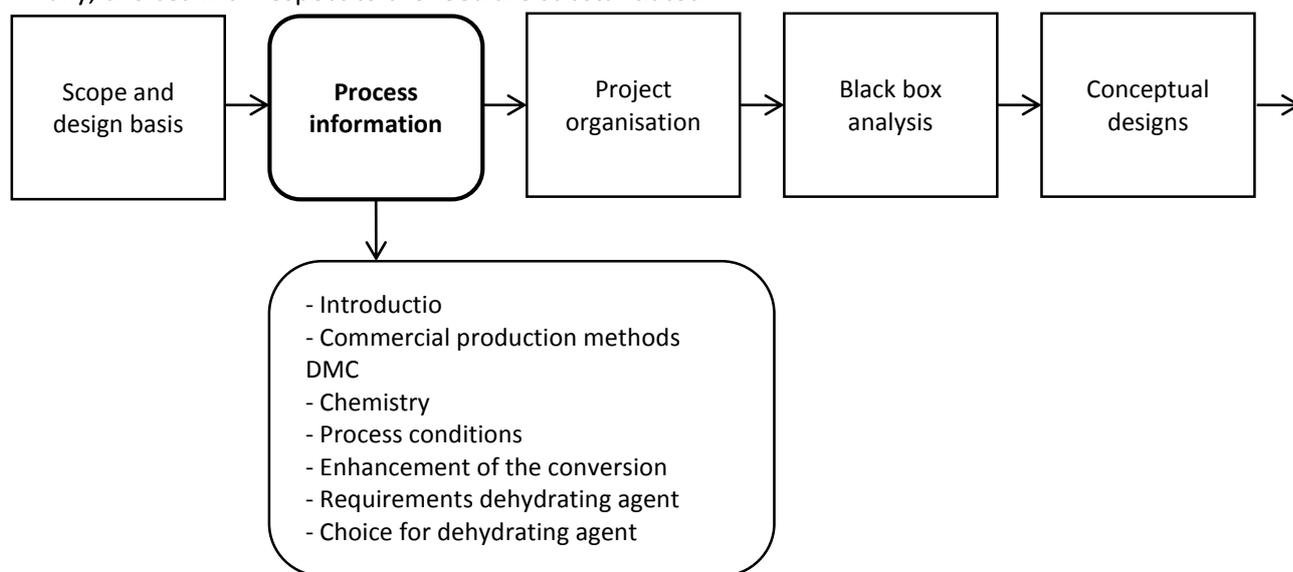
Table 1: Design specifications

	Property
Production capacity	450 ktpa
Purity	99.8%

## 2 Process information

### 2.1 Introduction

General process information about DMC production is given in this chapter. Information that forms the basis of a process and sets boundaries for the process. First, some insights in current ways to produce DMC are discussed. Then the chemistry of the reaction of interest is given. Furthermore, information about the catalyst and optimal process conditions are examined. Thereafter, ways to improve the conversion are discussed. In addition, the use of a dehydrating agent is further highlighted. Finally, choices with respect to the feed are substantiated.



### 2.2 Commercial DMC production methods

The next four production routes for the commercial production of DMC are identified[17, 18]:

1. Phosgene route, the oldest method to produce DMC;
2. Oxidative carbonilation route (including the nitric oxide route);
3. Epoxide route;
4. Transesterification route.

The main advantages and disadvantages of these production methods are summarized in Table 2 on page 12. Figure 2 clearly shows routes to produce DMC. It was not found that the route which includes urea is used commercially.

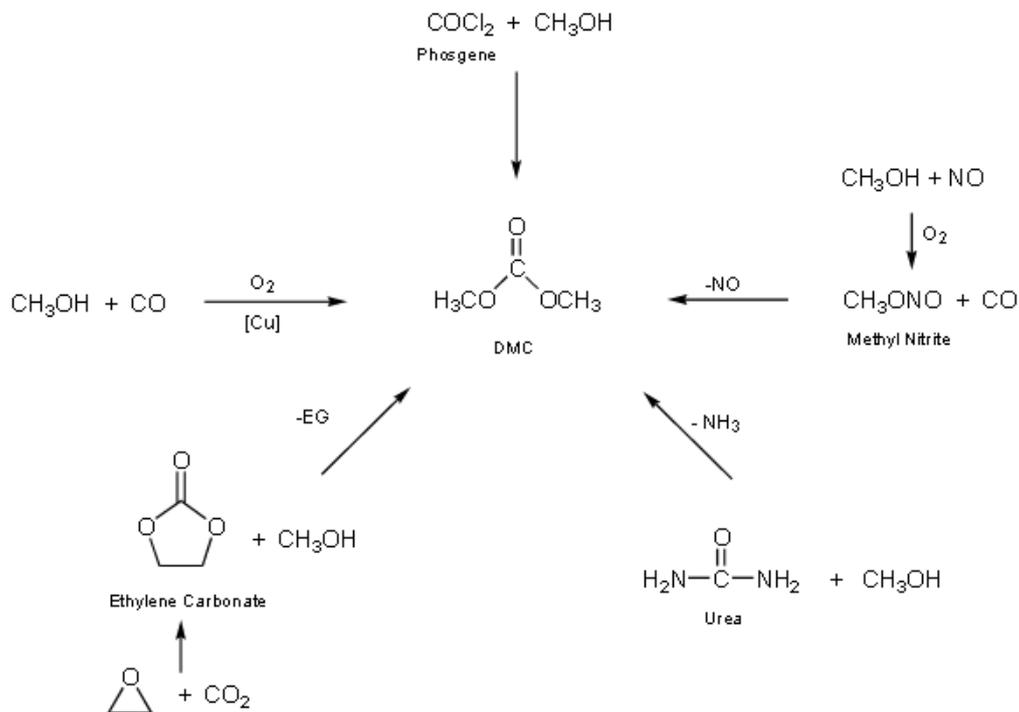
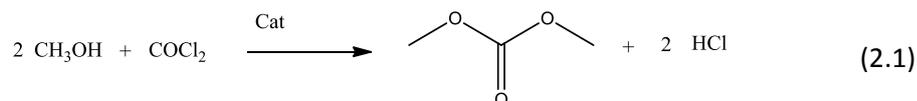


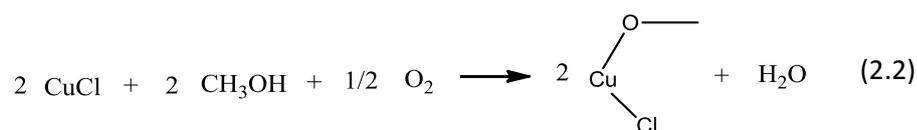
Figure 2: Overview of DMC synthesis routes. From: [19]

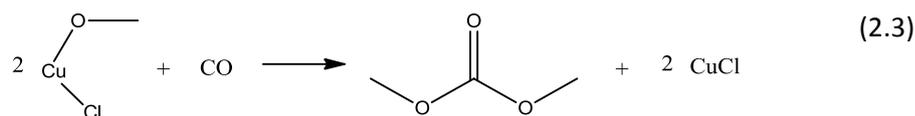
The phosgene route was widely used till the 1990's[20]. This method includes the next reaction:



An excess of methanol is used, which is later on distilled from the mixture. High purities are achieved by distilling the raw product. The purity is increased by adding a concentrated sodium hydroxide solution, which catalyses the reaction and increases the yield [21]. Different operating temperatures are found in literature, in the range between 253 - 313 K [17, 22] and 345 - 445 K [20]. When a Raschig ring-packed bed is used, it is possible to collect the HCl from the top of the column and the DMC from the bottom [20, 23].

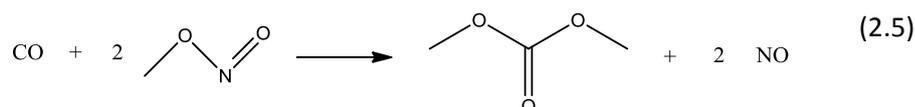
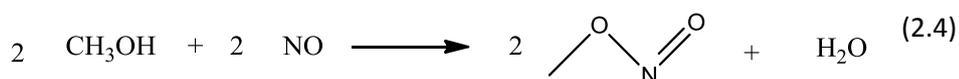
The presence of hazardous compounds as phosgene and HCl has shifted the focus to other types of reactions such as the oxidative carbonylation route [17, 22], which is currently one of the main methods to produce DMC [21, 24]. The oxidative carbonylation of methanol is performed via a homogeneous catalyst[21] and heterogeneous catalyst [25] by ENI in Ravenna (using a copper chloride slurry and with a capacity of 12 ktpa in 1993). In more recent work, ENI states that this production method has proven to have the capacity up to a 100 ktpa [22]. The reaction mechanism of the reaction includes the reactions:





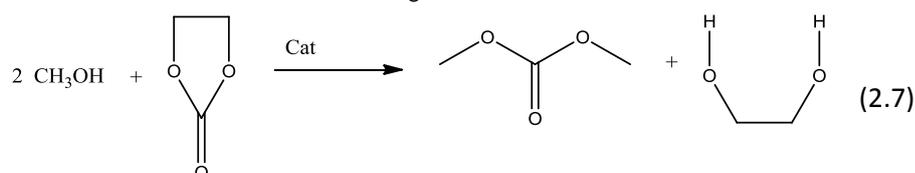
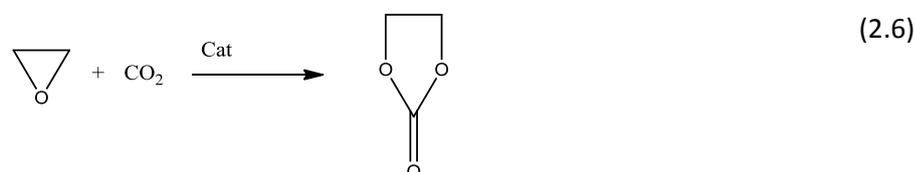
By-products that are formed during this reaction are CO<sub>2</sub> and minor amounts of dimethyl ether, methyl chloride and dimethoxy methane. [21, 22] Organic compounds are removed from the unreacted gasses and are purged afterwards. The gasses are sent to the CO recovery units, where the CO is recovered and recycled in the system. The mixture of DMC and unreacted compounds is sent to the acid recovery unit, where the HCl and catalyst are removed from the mixture. These are recycled. The DMC, water and methanol are separated via azeotropic distillation. A final purification step is added to remove the water from the DMC [21, 22, 26]. The operation conditions have an upper limit of 363 K and 100 bar [27]. A block flow diagram of this process, provided by CB&I is shown in Appendix C.1.

Oxidative carbonylation is also possible in the presence of nitric oxides, which is also referred to as the nitric oxide route. The nitric oxide route is applied by UBE for the commercial production of DMC with an initial capacity of 3 ktpa [21, 23]. This route includes the next reactions:



The process includes a catalytic reaction that is conducted in the vapour phase (see Appendix C.1 for the flow diagram). The produced DMC and excess methanol is adsorbed from the reactor effluent in dimethyl oxalate in an adsorption column. The unreacted gasses are sent to a regenerating column, where the gasses are mixed with oxygen containing gas and methanol in order to form methyl nitrite. This mixture is sent to the reactor. Methanol and DMC/dimethyl oxalate are separated by extractive distillation. Afterwards, the methanol is sent to a separate distillation column for further purification. The purified methanol is sent to the adsorption column for reaction. The DMC is separated from dimethyl oxalate by distillation, where the dimethyl oxalate is recycled to the adsorption column.

The epoxide route includes two steps: the production of cyclic carbonates via epoxides and CO<sub>2</sub>. Hereafter, a transesterification step with methanol yields DMC and glycol as a by-product [22].



Despite of the transesterification that occurs in the second step of the epoxide route, it is also seen as a separate route to produce DMC. The reaction mechanism remains the same.

The development of commercial feasible production methods is still emerging. In the last couple of years, the interest has shifted to the production of DMC by environmental friendly production methods. The same trend is seen in general, where the overall interest in green alternatives for chemical processes is emerging. At this moment, E3Tec Service, an engineering office/research facility, has already developed a commercially available process that uses methanol and CO<sub>2</sub> for the DMC production. It involves 'heat integrated reactive distillation' and is claimed to be very efficient, environmentally responsible and flexible enough to be integrated with major industry sectors. Unfortunately, more details about this process are unknown.[28]

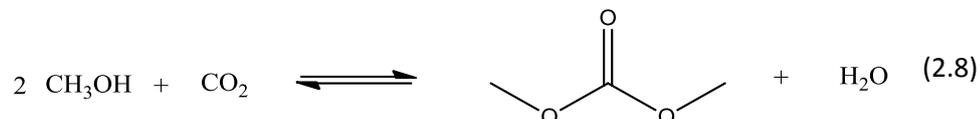
Table 2: Advantages and disadvantages of four DMC production processes. From: [18, 21, 29, 30]

	<b>Advantages</b>	<b>Disadvantages</b>	<b>By-products</b>
<b>Phosgene route</b>	High selectivity High yield	Use of phosgene Formation of HCl Corrosive resistance equipment is required	
<b>Oxidative carbonilation route</b>	Seen as an ecologically and economically feasible route	Low production rate Separation is expensive Large recycles are required Corrosive resistance equipment is required	CO <sub>2</sub> Dimethyl ether Methyl chloride Dimethoxy methane
<b>Epoxide route</b>	Forming of epoxides is a fast reaction, however, the transesterification is slow Additional revenues for selling ethylene glycol	Overall slow reaction Equilibrium limited reaction High pressures are needed Epoxides are expensive	Ethylene glycol (glycol : DMC = 1:1)
<b>Transesterification route</b>	Reaction mixture is non-corrosive and not dangerous Relative easy separation of reactants and products Additional revenues for selling ethylene glycol	Slow reaction Equilibrium limited reaction	Ethylene glycol (glycol : DMC = 1:1)

## 2.3 Chemistry

### 2.3.1 Reactions

The reaction of interest is the direct synthesis of DMC from CO<sub>2</sub> and methanol. The reaction scheme is given in equation (2.8). Besides DMC, also water is formed during this reaction. [6, 7]



Due to the Gibbs free energy of +26 kJ/mol, the reaction is equilibrium limited, which is the main drawback of this reaction. The methanol conversion from thermodynamics is expected to be less than 1%, even with favourable the process conditions. [7, 31]

Besides the formation of DMC, also formaldehyde and carbon monoxide are formed as by-products. This follows from equation (2.9). [32] The formed water can react with methanol to form CO<sub>2</sub> and hydrogen, equation (2.10). [33]



### 2.3.2 Catalyst

It has been reported that different kinds of catalyst show activity for this reaction. Among them are Cu – KF/MgO-SiO<sub>2</sub>[32], Cu – Ni[34, 35], metal oxide supported Rh[33], ZrO<sub>2</sub>[36] and CeO<sub>2</sub>[6, 7]. Different catalysts cause a different methanol conversion and DMC selectivity. A fair comparison is difficult, because all catalyst are used with different reactor set up and process conditions. Bansode et al. show the highest selectivity towards DMC with a CeO<sub>2</sub> catalyst, but a dehydrating agent is used to shift equilibrium. [7]

## 2.4 Process conditions

In literature a range of process conditions are used for this reaction. Also different catalysts are used, which may influence the optimal conditions to carry out the reaction. A list of process conditions and corresponding conversions can be found in Table 3. The selectivity towards DMC is similar in every research. The operating temperature varies at little, but overall a temperature around 120°C is the most used. For the pressure on the other hand, there are much more differences. In the first five researches mentioned in the table the pressure is relatively low, but in the latter two the pressure is higher. This increasing pressure is probably applied to shift the equilibrium towards the products. [7, 31, 32, 34-36]

Table 3: Overview of process conditions used in literature

Author	Catalyst	Pressure (bar)	Temperature (°C)	Feed ratio (MeOH/CO <sub>2</sub> )	Conversion (%)	Remarks
Li et al. (MCR)[32]	Cu-KF/MgSiO	4	130	2	8 – 9	Membrane reactor
Li et al. (CCR)[32]	Cu-KF/MgSiO	1 – 12	80 – 140	1.5 - 3	2 – 5	
Bian et al.[35]	Cu-Ni/TEG	12	100	2	5	Thermally expanded graphite support
Chen et al.[34]	Cu-Ni	11	120	0.1	7.2	Molecular sieves
Tomishige et al.[36]	ZrO <sub>2</sub>		140 – 200	0.96		
Honda et al.[6]	CeO <sub>2</sub>	50	120	100mmol / 5MPa	94	Dehydrating agent
Bansode et al.[7]	CeO <sub>2</sub>	1 – 300	80 – 160	0.4	95	Dehydrating agent

## 2.5 Enhancement of the conversion

To enhance the conversion, the equilibrium must be shifted towards the products. Besides changing temperature and pressure, this can be done by developing a novel strategy to remove one of the products. In literature several methods are proposed to increase the conversion. They all have the same basis, namely the removal of water from the reaction mixture. An overview of options to remove water from the reactor are provided in Appendix C.2.1. A brief summary is given below.

Four methods are reported to enhance the reaction towards DMC;

- A membrane reactor,
- Molecular sieves,
- Reactive distillation,
- A dehydrating agent.

From these methods, a dehydrating agent is selected to be the best option to enhance the reaction. Membrane reactors do not achieve a high enough conversion [32]. Molecular sieves operate at a different temperature than the DMC synthesis and an internal recycle is not efficient enough [37]. Reactive distillation is not an option with the compounds involved in the reaction, because the two products are the highest boiling compounds in the reaction system. The use of a dehydrating agent on the other hand shows high methanol conversion and a high selectivity is remained. From the numerous dehydrating agents tried out for DMC synthesis, 2-cyanopyridine seems the most suitable. [7]

However, further research has concluded the crucial step of regenerating the dehydrating agent is not feasible with the selected agent. It is technically possible, but takes too much time to be used in industrial applications [6, 38, 39]. An extensive literature study has been carried out to find potential dehydrating agents, but these agents are not reported in combination with the direct synthesis of DMC. The list consists of organic compounds, formates, salts, MOF's and enzymes. From these, most of the dehydrating agents are not possible in combination with the DMC synthesis, either the process conditions are not similar, an aqueous environment is needed, regeneration is an issue or the reaction does not coincide the goal of this research. [40-44]

## 2.6 Requirements dehydrating agent

To select a good dehydrating agent, a list of requirements for the agent was set up. Obviously, the goal of the agent is to remove water, and therefore the compound should react with water. It should be powerful enough to do this. Thus, it should already react with water when there is only a very small amount of water. In addition, it should do this sufficiently fast enough. What hereafter is important, is the ability to do this at favourable operating conditions. The aim is to operate the reactor at a temperature of 120°C as is mentioned in paragraph 2.4. The pressure was not chosen yet, because a wide range for the pressure is suitable. Another key aspect of the agent is its recoverability or it should be very cheap so that one time use is still economically feasible. In addition, there are requirements that not necessary have to be fulfilled but can result in problems. To summarize, the requirements are listed below with bullet points.

- React with water (chemical or physical)
- Reaction with water significantly powerful
- Reaction with water significantly fast
- Able to react within operating window
- Recoverable, or very cheap
- No or negligible side reactions
- Available at significant quantities
- Not corrosive

## 2.7 Choice for dehydrating agent

Various dehydrating agents examined against the list of requirements. 2-Cyanopyridine is a promising dehydrating agent for this process, as is stated before in this report. Actually, the article of Bansode et al. was the motive for this research [7]. However, the problem with this agent is that little knowledge is available about the recoverability of 2-cyanopyridine. It was reported by Honda et al. that it is possible to recover 2-picolinamide back to 2-cyanopyridine [6]. However, the time needed for 90% conversion is about 500h.

Therefore, other compounds were checked on suitability to act as a dehydrating agent. An extensive list with dehydrating agents with their pros and cons is listed in Appendix C.2. For example, salts, such as CaO and MgO were interesting in a first impression. However, these salts favour a reaction with CO<sub>2</sub> above the reaction with water (take into account the CO<sub>2</sub> rich atmosphere in the reactor). Salts such as MgCl<sub>2</sub> and CaCl<sub>2</sub> give the problem that they do not react significantly enough with water at favourable operating temperatures. Organic compounds in general give the problem that they do not react with water at the operating temperature, need an acid catalyst in water or are very likely to give various by-products. The by-products are a result of the reactivity with methanol and a lot more methanol is present in the system compared to water.

In conclusion, 2-cyanopyridine was chosen as the dehydrating agent for the process. Further research about the recoverability is needed, but no other compound with similar potential could be found. Advantage is also that 2-cyanopyridine was tested in combination with the reaction to produce DMC, with high conversion and selectivity.

## 2.8 Feed composition

The CO<sub>2</sub> feed added to the reactor can come from various sources. The composition depends strongly on the source. The various sources that can be used are: air, flue gas from a power plant or pure CO<sub>2</sub> can be purchased. The concentration of CO<sub>2</sub> in air is much too low (400 ppm) to efficiently capture CO<sub>2</sub> from in an industrial scale [45].

The composition of flue gas from gas and coal power plants is given in Table 4.

*Table 4: Flue gas compositions of gas and coal power plants. From: [46]*

	<b>Coal</b>	<b>Gas</b>
<b>CO<sub>2</sub></b>	12.8%	7.5%
<b>H<sub>2</sub>O</b>	6.2%	14.5%
<b>N<sub>2</sub></b>	76.6%	74%
<b>O<sub>2</sub></b>	4.4%	4%
<b>CO</b>	0.005%	0.03%
<b>SO<sub>2</sub></b>	0.042%	-
<b>NO<sub>x</sub></b>	0.042%	0.007%

Of course these values are not set in stone, but they give a good indication of the usual compositions of flue gas. Water and oxygen are catastrophic in the reactor due to the potential burning of methanol and the effect of the water on the equilibrium. It will therefore be necessary remove these impurities. The effects of the other compounds on the reaction system are unknown, but it is very likely that the sulphur dioxide will poison the catalyst. Based on these considerations, it is decided to use pure CO<sub>2</sub> as feed stream. Either bought or purified on site from one of the other sources.

Methanol is primarily produced from synthesis gas from natural gas. For the production it is beneficial to have a H<sub>2</sub>/CO ratio just above 2 and thus it is best to use methane as the only component to produce the synthesis gas [47]. This makes it clear that most of the methanol is produced from fossil fuels. However, the synthesis gas can also be produced from biomass; this would lead to much more complications, primarily related to the composition of the gas. The result is usually a gas with a much higher carbon monoxide concentration. This could be overcome using the shift reaction, but this would lead to lower value of the product stream due to the high CO<sub>2</sub> content [47].

Other methods for the production of methanol are the direct hydrogenation of CO<sub>2</sub>. This was investigated a lot in the 90's, but it is still in development and thus not a reliable source [47]. Also no hydrogen source is present at the plant and the transport of hydrogen will be costly. Direct oxidation of methane is also a method. But this method is kinetically and thermodynamically very unfavourable and thus is not used in industry yet either [47].

Based on these considerations it can be concluded that the production of methanol that is bought for use in the plant is probably from fossil fuels. However, this would interfere with the sustainability goal set in the scope. Therefore, the intention is to use bio-methanol to run the plant. In this report the assumption of pure methanol as feed stream is used.

## 2.9 Summary

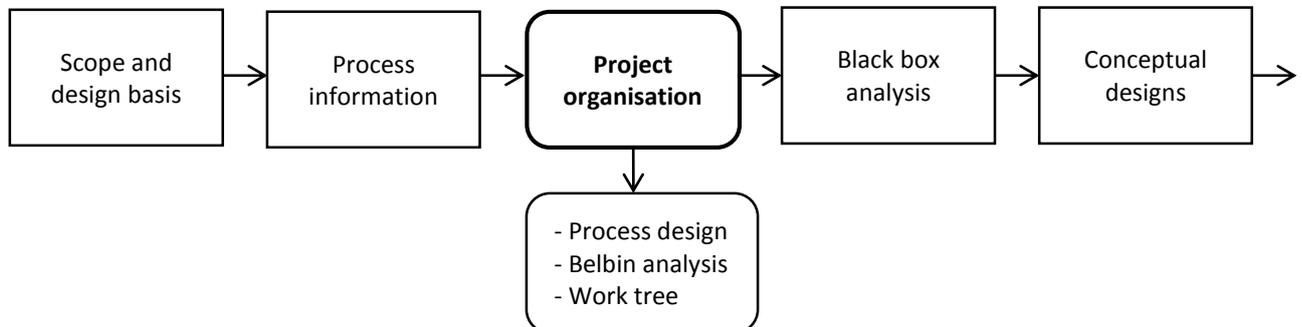
The production process of DMC based on a green route with a feedstock of methanol and CO<sub>2</sub> is considered. Methanol and CO<sub>2</sub> are assumed to be pure, when it enters the process. The drawback of this reaction is the equilibrium. From thermodynamics the maximum conversion is less than 1%, thus a novel strategy to shift the equilibrium should be developed. Different dehydrating strategies were considered, wherefrom the use of dehydrating agent is considered as the one with the most potential. All kinds of agents were evaluated and 2-cyanopyridine was chosen. It shows a significant enhancement of the reaction and the selectivity towards DMC remains very good.

Some research has been carried out in recovering the dehydrating agent, an important step in the process. The speed at which this be recovered is a problem (>400 h) en should be further investigated by the scientific world.

Optimal reaction conditions are found to be 30bar and 120°C. Then the conversion can be 92.4% and selectivity 99%. In this system a CeO<sub>2</sub> catalyst is used, because it can activate both the direct synthesis of DMC and the dehydration reaction.

### 3 Project organisation

Many different methods could be applied to organise a large project. Within this chapter, the organisation method that is used during this design project is discussed. This also includes a bar chart planning which is provided by Appendix D.1 and a Belbin team role analysis, which is briefly discussed in the last section of this chapter.



#### 3.1 Process design

The main goal of this project is clear: designing a DMC plant based on some basic information on input and output. The method that is used to organise this project is based on the hierarchical decision procedure of Douglas. A brief description of this method is given in Appendix D.2.

To provide a clear overview on the work that has to be performed, a work tree is made (see Figure 3, page 20). The tree should give an overview of what was done, when it was done with respect to other tasks (in parallel or after one part was finished) and the choices that were made (not why they were made).

#### 3.2 Belbin analysis

Apart from discussing the planning and project organisation, it is also important to know which type of people are involved in the team. For this reason, a Belbin analysis is done (see Appendix D.3) for all the details). The PPD207 project group (4 team members) includes five out of the nine Belbin team roles. Many team roles overlap between the team members, such as the implementer, monitor/evaluator and complete finishers. One team member is also a shaper and another team member has the characteristics of a specialist. The most important team role that is missing is the coordinator, which might result into planning and execution issues.

Anne quits the project after about the first half of the project due to personal reasons. The team continues with the remaining three members. Therefore, the group should compensate for the roles of Anne. As the project is time wise now about half way, and the group members know each other quite well this should not result in problems, besides the fact that one group member and the corresponding working hours are missing.

#### 3.3 Summary

Douglas' hierarchical decision procedure is used for the design of a DMC plant. This method includes different levels and at each level more detail is included. This has the advantage that it is relatively simple to create an overview of choices and alternatives. An overview of the work that has to be performed during the design of the DMC plant is shown in Figure 3.

Another important part of the project organisation, is the identification of the different types of persons that are in the team. The project group includes five out of the nine team roles defined by Belbin (see also Appendix D.3). Three of these roles (the implementer, monitor/evaluator and complete finisher) can be assigned to two or more team members.

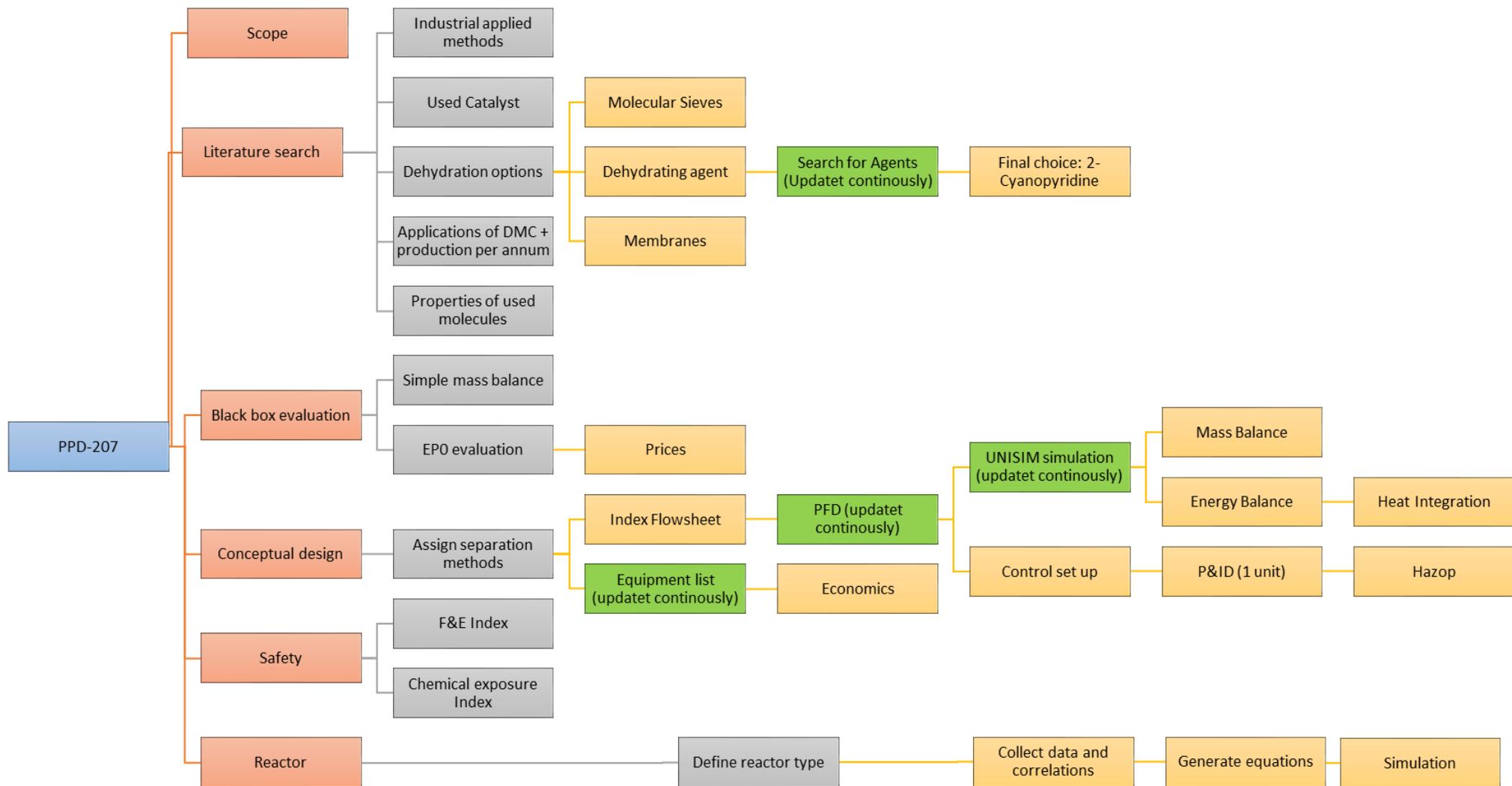
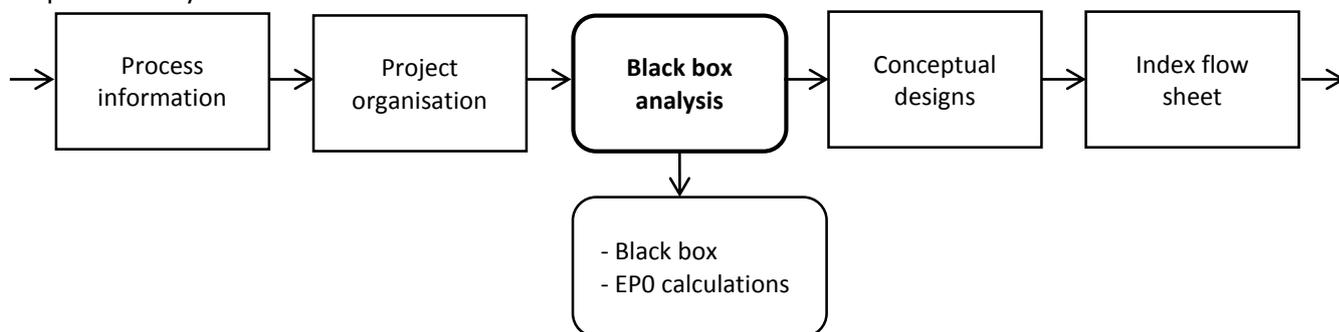


Figure 3: Overall work diagram for project PPD 207, boxes in green were constantly evaluated and changed

## 4 Black box analysis

In this chapter black box, a simple mass balance and EP<sub>0</sub> pricing are considered. A very first view on the needed capacity and a simple economic evaluation is made. In addition, the break-even point with respect to the yield is calculated.



### 4.1 Black box

DMC is produced by a reaction of methanol and CO<sub>2</sub>. To give a very first estimate whether this process could be economically feasible, a so called black box calculation is done. The black box for this process can be seen in Figure 4. The use of 2-cyanopyridine (C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>) as a dehydrating agent is incorporated in the calculations.

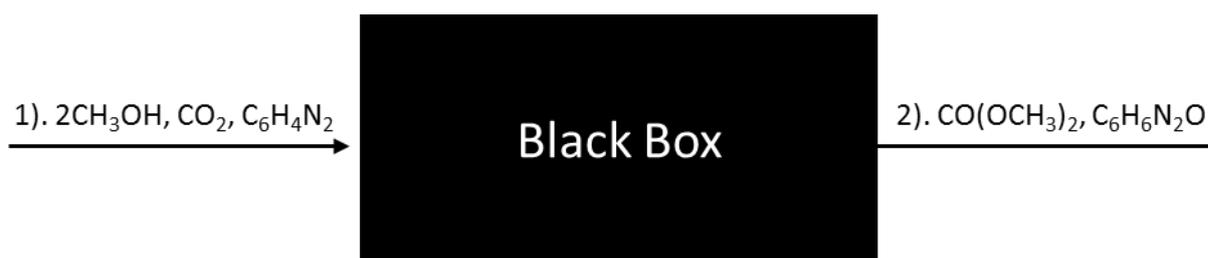


Figure 4: Black Box for DMC production from methanol and CO<sub>2</sub>

The mass and molar flows are calculated by assuming an annual production of 450ktpa. The results are shown in Table 5. On the basis of this simple mass balance a first estimate of the economic feasibility is made. Prices for the compounds are shown in Table 6. Assumptions about selectivity and conversion are based on the article of Bansode et al. [7]. They report a selectivity towards DMC of 99% at the desired operating conditions, also the selectivity of 2-cyanopyridine towards 2-picolinamide (C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O) is 99%. The implementation of a recycle can improve the conversion to 100%.

This results in a profit of 229\$ per ton of produced DMC, with a production goal of 450ktpa this would result in a revenue of 103 million per annum. However, capital and operation costs are not taken into account, but this gives an indication that the development of such a process seems economically feasible at this stage. The price for CO<sub>2</sub> is estimated at 5\$ per ton. In general, the emission of CO<sub>2</sub> results in a penalty, therefore technically the price could be negative. However, purifying streams that contain CO<sub>2</sub> to a high concentration (>99%) of CO<sub>2</sub> also costs money. An equal amount of 2-cyanopyridine is needed with respect to DMC on molar basis, however the ratio in price per mole is about 15 as can be seen from Table 6. Therefore, the loss of agent should be minimised at all cost.

Table 5: Mass and mole balance for black box analysis

[kmol/year]	1).	2).	[kg/year]	1).	2).
CH <sub>3</sub> OH	9.99E+06	0	CH <sub>3</sub> OH	3.20E+08	0
CO <sub>2</sub>	5.00E+06	0	CO <sub>2</sub>	2.20E+08	0
CO(OCH <sub>3</sub> ) <sub>2</sub>	0	5.00E+06	CO(OCH <sub>3</sub> ) <sub>2</sub>	0	4.50E+08
H <sub>2</sub> O	0	5.00E+06	H <sub>2</sub> O	0	9.00E+07

Table 6: Prices of compounds.

Compound	Price (\$/ton)	Price (\$/mole)
CH <sub>3</sub> OH <sup>[48]</sup>	500	0.16
CO <sub>2</sub> <sup>[49]</sup>	5	0.002
CO(OCH <sub>3</sub> ) <sub>2</sub> <sup>[50]</sup>	700	0.63
H <sub>2</sub> O	0	0.00
C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> <sup>[51]</sup>	9150	9.53

## 4.2 EP<sub>0</sub> evaluation

In the black box calculation with respect to the economic feasibility a conversion and selectivity of 100 % are taken. However, in reality this is most of the time not the case. Usually a conversion of 100 % is achieved in a process, sometimes the implementation of a recycle is needed for this. Therefore all raw material is converted to products, and thus only the selectivity is relevant for the yield. The profit per ton of produced DMC with respect to the yield at 100% conversion is shown in Figure 5.

This results in a break-even point at a yield of 0.51. No side reactions are taken into account, because these depend on unknown factors such as catalyst type and operating conditions. As a result, no money is generated from the formation of side products. However, this could be the case and the break-even point could even be lower. However, also the opposite might be true. It could cost money to get rid of the side products.

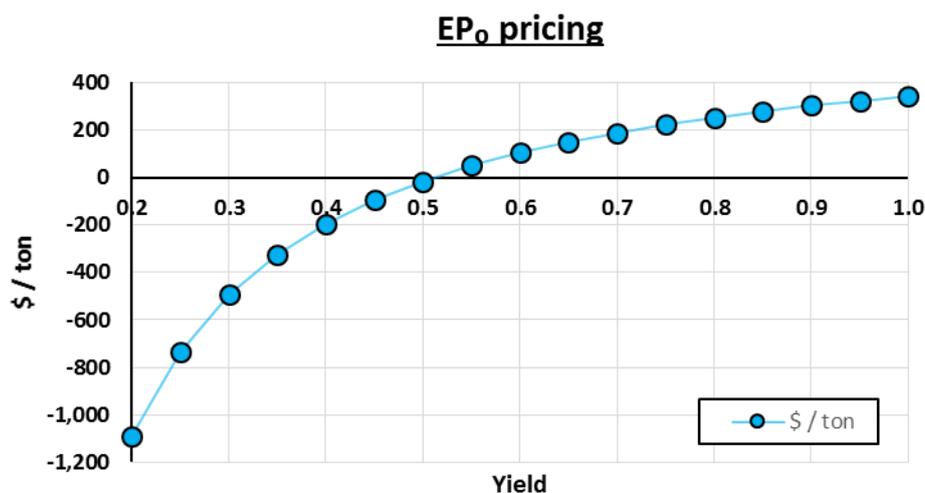


Figure 5: EP<sub>0</sub> profit per ton of DMC produced with respect to the yield at 100% conversion, dehydrating agent not taken into account

In Figure 6 the influence of the loss of dehydrating agent versus the revenue per ton DMC produced is plotted. This is done because the agent is much more expensive than the other compounds. Figure 6 also shows that the recovery of the agent is crucial to make the process economically viable. Already a loss of 3.2% of the agent in the process would result in a break-even point. However, possible sales of side products that are formed from the agent that is lost are not taken into account.



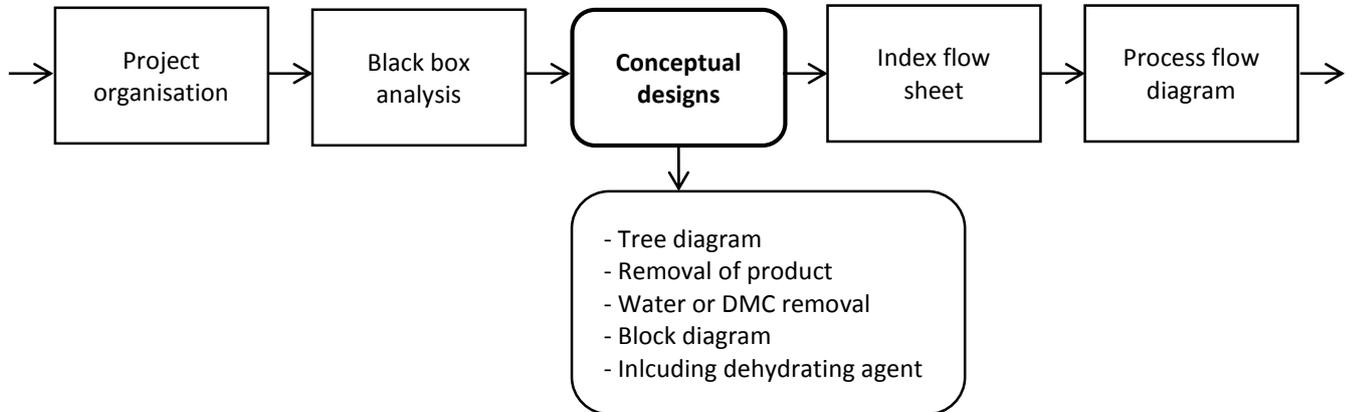
Figure 6: Revenue per ton DMC produced with respect to the loss of agent (Selectivity towards DMC = 99%), 100% conversion

### 4.3 Summary

For the production of 450ktpa of DMC 323 ktpa of methanol and 222ktpa of CO<sub>2</sub> are required at 100% conversion and 99% DMC selectivity, assuming that 1% of the agent is not recovered. This would result in a profit of 229\$ per ton of produced DMC, thus a revenue of 103million per annum. Recovery of the agent is crucial. When assuming 100% conversion, which can be achieved by a recycle, a minimum selectivity of 51 % is needed for break even (Influence of agent is not taken into account here).

## 5 Conceptual design

Conceptual designs are developed for this process, starting with the black box from Chapter 4. Within this black box the necessary reaction and separation steps will be identified. In addition the recycles are included in the designs. If the recycle contains a gas then also the compressor is shown, because this could be a key factor due to its high costs.



In this chapter the choice for the conceptual design is made according to the decision tree (Figure 7). Every step in the tree will be discussed in a different section using both the theory of chapter 2 and global mass balance. All conceptual designs can be found in Appendix E.1.

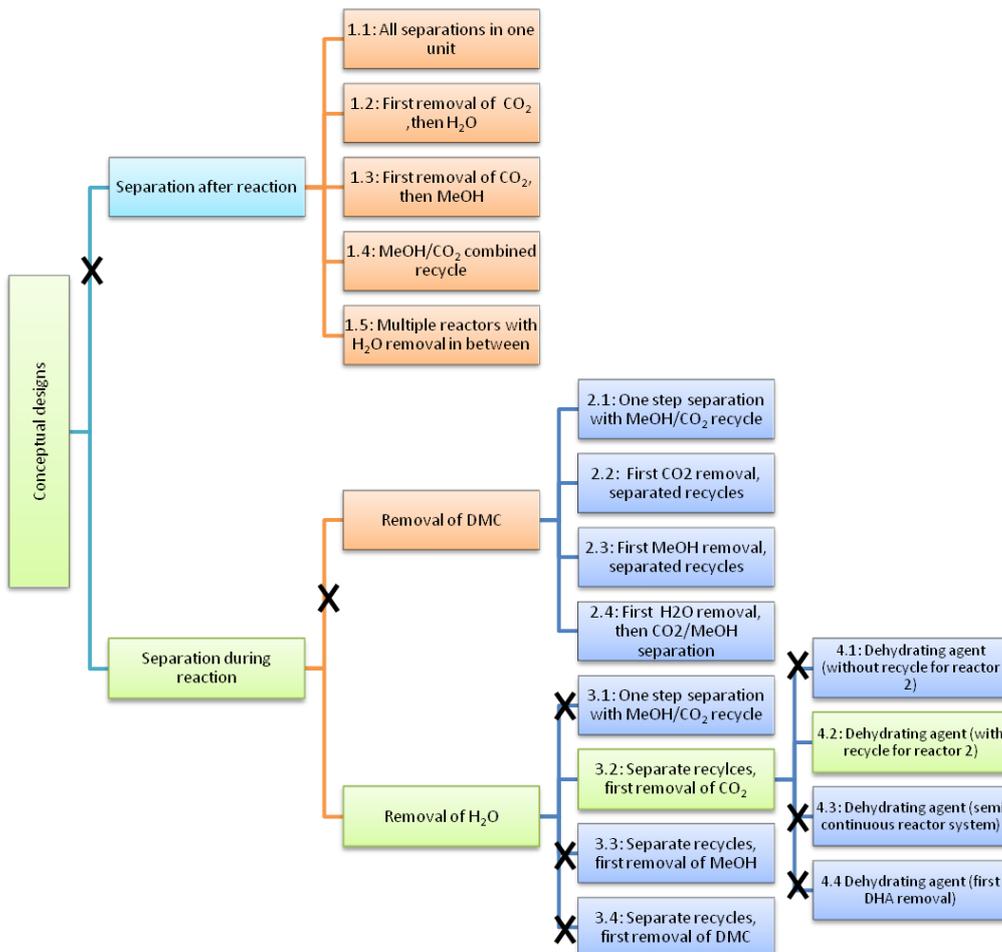


Figure 7: Decision tree for conceptual designs

## 5.1 Removal of product

As shown in the decision tree, there are two major approaches for this process. Either the separation of one of the products occurs after the reaction or separation occurs during the reaction. The direct synthesis of DMC from CO<sub>2</sub> and methanol is very unfavourable from a thermodynamic point of view, therefore it might be beneficial to remove one of the products and enhance the conversion. The reaction without in situ removal of one of the products in the reactor reaches equilibrium below 1% conversion according to thermodynamics [52, 53], but other sources state that they have reached conversions up to 7% without any removal of the products, but with the use of complex catalysts [34, 54]. Due to the single pass conversion being much higher with the removal of products, the recycle back to the reactor is much lower and thus would lower the separation, gas recycle and pump utilities enormously [7, 55]. Therefore, the removal of the products inside the reactor is the preferred method for the production of DMC. In case later on it is ascertained that in situ removal of a product is not possible, conceptual designs 1.1 until 1.5 are made for the separation section after the reaction. Conceptual designs 1.1, 1.2, 1.3 and 1.4 just have a different separation sequence, where 1.5 has an interstage removal of H<sub>2</sub>O.

## 5.2 Water or DMC removal

As there are two products, a choice should be made which of the products is most suitable to remove during the reaction. In chapter 2 the different methods to remove water are mentioned. Four methods are described in literature: a membrane reactor, molecular sieves, reactive distillation and a use of a dehydrating agent. So, it is possible to remove water from the reaction mixture and enhance the conversion. [7, 32, 37, 56, 57]

The removal of DMC from the reaction mixture is not described in literature. It is probably more convenient to remove water, with membranes or chemical reaction for example. DMC is the desired product, so anything that will lower the selectivity towards DMC (a chemical reaction with a dehydrating agent for example) is not a desired method. In addition, no technology is known that is capable of selectively removing DMC.

Therefore, the choice is to remove water during the reaction, again some conceptual designs are made for the removal of DMC in case it turns out that removal of DMC in the reactor is the better option (2.1 until 2.4). The difference is again the sequence of compound removal. Also an option is available to combine the recycles of methanol and CO<sub>2</sub>.

## 5.3 Block diagram

For the removal of water during the reaction, some conceptual designs are made. Because water is removed during the reaction, only DMC, methanol and CO<sub>2</sub> will leave the reactor. Four different ways of separating them are presented (3.1 till 3.4). The first is a one step separation with a combined recycle of methanol and CO<sub>2</sub>, the others have separate recycles and a different order of separation.

Considerations that can influence the choice for a conceptual design are:

- First separate off the largest stream;
- Easy separations first;
- Choice between separate or combined recycles of CO<sub>2</sub> and methanol. CO<sub>2</sub> is an easy separation, but then separate recycles are needed and remixing occurs in the reactor;
- DMC/methanol form an azeotrope;
- Water/DMC form an azeotrope;

- Recycling DMC to the reactor, this will then be mixed with the methanol recycle. This can be considered if the methanol recycle is small and/or the DMC fraction is small compared to the feed.

Also a global mass balance is made to help with the decision, this can be found in Appendix E.2. The interesting part for this stage of the decision tree is at the outlet of the reactor. Due to the excess of CO<sub>2</sub>, this is the major fraction of the stream. At a reasonable conversion, there is little methanol left and quite some DMC. CO<sub>2</sub> is relatively easy to separate and is the biggest stream. Therefore it is best to get rid of this first and recycle it to the reactor. After that methanol and DMC are separated, the drawback is the difficult separation between these compounds and that methanol and CO<sub>2</sub> are mixed again in the reactor. This means that conceptual design 3.2 is chosen.

#### 5.4 Including dehydrating agent

In chapter 2 the different methods of water removal during the reaction are discussed and evaluated. It was concluded that the use of a dehydrating agent is the best option. Therefore, the conceptual design chosen in the previous section has to be extended.

A dehydrating agent can be added to the reactor and mixed with the reaction mixture or it is present inside the reactor. If it is a heterogeneous dehydrating agent then the reactor has to operate alternately as reactor for the DMC synthesis and regeneration of the dehydrating agent. This leaves to conceptual design 4.3.

If a homogeneous dehydrating is used, then an additional separation step to separate the dehydrating agent is needed. This stream will consist of reacted agent and unreacted agent and needs to be regenerated to obtain a pure stream of dehydrating agent again. Two designs are developed for this. One with a recycle to the regeneration reactor (conceptual design 4.2) and one without a recycle (conceptual design 4.3), this will depend on the conversion of the reactor.

A last option is to recover the dehydrating agent as quickly as possible. In this way the loss of dehydrating agent can be minimized. The first two separation steps are then switched compared to conceptual design 4.2.

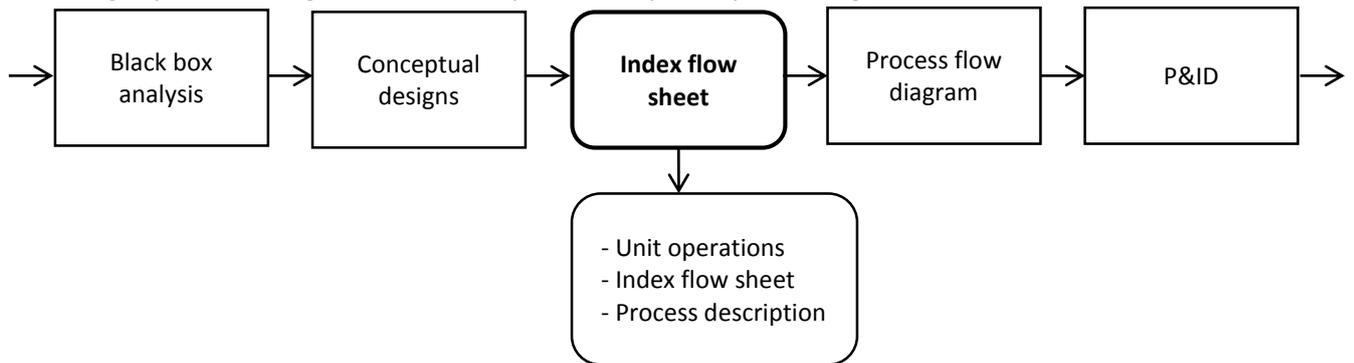
To make a decision, the dehydrating agent must be known. In chapter 2 it is decided that 2-cyanopyridine will be the dehydrating agent. This is a liquid at the process conditions and is mixed with methanol. Therefore, design 4.3 is not suitable for this process. The regeneration is a problem with 2-cyanopyridine. As stated in chapter 2, not much is known about this part, but an assumption can be made that the conversion will not be good enough to operate without a recycle of 2-picolinamide. The only part to choose is the compound to be separated first. Here the best option is probably to separate CO<sub>2</sub> first, it is both an easy separation and the largest fraction, but a more detailed process simulation is needed to make the final decision.

#### 5.5 Summary

In this chapter the conceptual design for the direct synthesis of DMC is developed. This reaction is enhanced by removing one of the products. Conceptual designs are made for both DMC and water. Concluding from the literature obtained in chapter 2, water is the best option to remove. From the four options, 3.2 is chosen as the best one based on the global mass balance. With the knowledge that 2-cyanopyridine will be the dehydrating agent, the conceptual designs are extended. Conceptual design 4.2 is the best option, although 4.4 is a good alternative.

## 6 Index flowsheet and process description

In this chapter the chosen conceptual design is developed into an index flowsheet. First the possible unit operations for the separation steps are discussed, whereupon the index flowsheet is made. A detailed process description is provided for this index flowsheet. In Appendix F.2 a decision tree is made for the unit operations. It is highly recommended to read this chapter with the PFD at hand. A decision tree for detailed separation choices is found in Appendix F.3 Tables that are shown in this chapter are used for comparison and to make choices. It might be that final specifications of equipment differ slightly due to integration (for example, more optimal preheating) or extra restrictions.



### 6.1 Unit operations

Conceptual design 4.2 is chosen as the best of the alternatives for this process. For each separation step, the possible separation techniques are listed. A short overview is given in Appendix F.2 in a decision tree. A work diagram which explains the steps taken to assign a unit operation to a separation step is shown in Figure 8. UNISIM simulation results are used to underpin decisions with respect to unit operations. Detailed information about UNISIM such as the choice for a fluid package can be found in Appendix F.1.

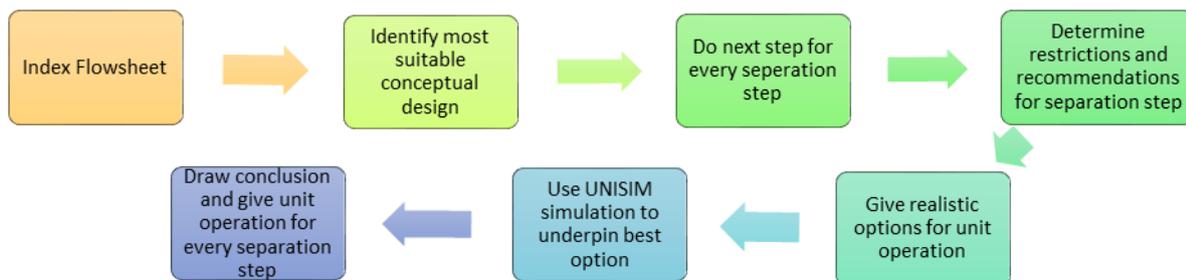


Figure 8: Work diagram to assign unit operations

### 6.1.1 S1 and S2

The first thing to decide is the sequence of the first two separations steps, the removal of CO<sub>2</sub> and the removal of (reacted) dehydrating agent. Thus, there are some possibilities concerning this separation and the following considerations are important:

- 2-picolinamide has a high melting point. Thus a high temperature (>110°C) is required when large quantities of this compound are in the system to avoid solid formation.
- Solubility of 2-cyanopyridine and 2-picolinamide in DMC and methanol is unknown. However, it is assumed that they will dissolve when these compounds are present in minor or trace amounts.
- CO<sub>2</sub> is recycled to the reactor, therefore any pressure release of CO<sub>2</sub> needs to be compensated in the compressor in the recycle stream.
- Due to the high value of 2-cyanopyridine and 2-picolinamide, they should be recovered as quickly as possible. Otherwise, small amounts of these compounds are lost in the separation step(s) before these compounds are separated from the mixture.

#### 6.1.1.1 S1 (Separate CO<sub>2</sub> from the mixture)

The approach is not to speculate about what happens when either of the two separation steps is done first, but simulation results of UNISIM are used to make a good decision. The conditions of the stream after the reactor are 120°C at 30bar. The temperature cannot be lowered due to possible solid formation as stated before. Release of pressure is unwanted due to increase of compressor duty for the CO<sub>2</sub> recycle. Therefore, a simple phase separation is carried out at the mentioned conditions. Results of the simulation of this phase separation are shown in Table 7. To show the influence of pressure on the separation, the results of a simulation at 1bar are also shown.

Table 7: Component mole fractions for flash separator (F-2071) at indicated pressures and 120°C

	<b>7</b>	<b>8</b>	<b>9</b>	<b>8</b>	<b>9</b>
	<b>(Reactor</b>	<b>(Bottom)</b>	<b>(Top)</b>	<b>(Bottom)</b>	<b>(Top)</b>
	<b>output)</b>	<b>30bar</b>	<b>30bar</b>	<b>1bar</b>	<b>1bar</b>
<b>Methanol</b>	0.03	0.05	0.02	0.01	0.03
<b>DMC</b>	0.17	0.40	0.05	0.08	0.20
<b>CO<sub>2</sub></b>	0.61	0.03	0.93	0.001	0.77
<b>2-Cyanopyridine</b>	0.01	0.04	0.0002	0.05	0.004
<b>Picolinamide</b>	0.17	0.48	0.0001	0.86	0.001
<b>Total flow</b>					
<b>(kmol/h)</b>	3585	1362	2223	761	2824

Operating the flash separator at 30bar shows that the vapour stream (9) is almost free from the agent compounds. Therefore, this stream which is then already quite pure in CO<sub>2</sub> (93 mole% mole fraction) can be processed further without the risk of solid formation at a lower temperature. The stream in the bottom is still a mixture wherefrom the amount of CO<sub>2</sub> is significantly reduced.

For operation at 1bar there are no significant advantages. The bottom stream (8, 1bar) with the agent compounds is more pure, but far from highly pure. As a result, the top stream (9, 1bar) is even less pure and significant amounts of agent are in this stream (0.5 mole% fraction in total). In addition, reducing the pressure reduces the temperature, which is known as the Joule-Thomson effect. Thus the

pressure reduction must take place stepwise with heating in between to avoid a temperature lower than 110°C.

Concluding, it makes no sense to do the phase separation at reduced pressure. However, the vapour stream is not highly pure in CO<sub>2</sub> and needs to be further processed before it is recycled to the reactor. This is simple done by cooling the stream followed by a second flash separator, which is now possible. In this fashion a very large amount of the CO<sub>2</sub>, which is used in excess, is removed in two simple steps, still maintaining a pressure of 30bar.

Table 8: Component mole fractions for second flash separator (F-2072) at about 30bar and 20°C

	9	10 (Bottom)	11 (CO <sub>2</sub> recycle)
<b>Methanol</b>	0.02	0.19	0.004
<b>DMC</b>	0.05	0.64	0.004
<b>CO<sub>2</sub></b>	0.93	0.16	0.99
<b>2-Cyanopyridine</b>	0.00	0.00	0.00
<b>2-Picolinamide</b>	0.00	0.00	0.00
<b>Total flow (kmol/h)</b>	2223	155	2068

The results of the second flash separator, which operates at 20°C, are shown in Table 8. It shows that the vapour stream is highly pure in CO<sub>2</sub> (>99 mole%). The presence of methanol is irrelevant, because methanol is also recycled to the reactor. Only the presence of DMC is disadvantageous for the reactors efficiency, however the amount is very small (0.4 mole%). The recovery of CO<sub>2</sub> by these two flash separators is 97%.

Summarizing, S1 is a combination of 2 flash separators for the removal of CO<sub>2</sub>.

#### 6.1.1.2 S2 (Separate 2-cyanopyridine and 2-picolinamide from the mixture)

S2 is the separation step which has the goal to separate 2-cyanopyridine and 2-picolinamide from the mixture. Starting point for S2 is the liquid stream of the first flash separator, see Table 7 stream 8 (bottom, 30bar). The reason to place this separation step relatively early in the process is that the recovery of agent is crucial due to its high value.

There are different possibilities to separate the agent and the reacted agent from the mixture. Though, there are some uncertainties with respect to 2-cyanopyridine and 2-picolinamide because not all properties are known or some sources are contradictory. Melting and boiling points of the compounds in the feed for S2 are displayed in Table 9, besides the molar fractions are given. Crystallization can possibly be an option to separate 2-picolinamide (mp = 110°C) from the mixture. However, this also depends on the solubility of 2-picolinamide in the other compounds, mainly DMC, which is unknown. Let alone that phase diagrams for this system are available. In addition, solid formation process should be avoided if possible, due to transportation issues.

Table 9: Melting and boiling points of compounds relevant for S2 at atmospheric pressure and mole fractions of compounds in the stream, \*CO<sub>2</sub> doesn't have a mp or bp but a sublimation point (at atmospheric pressure) [58-60]

	<b>Mp (°C)</b>	<b>Bp (°C)</b>	<b>Fraction (mole%)</b>
<b>Methanol</b>	-98	65	0.05
<b>DMC</b>	1	90	0.40
<b>CO<sub>2</sub></b>	-79*		0.03
<b>2-Cyanopyridine</b>	27	213	0.04
<b>2-Picolinamide</b>	110	284	0.48

Techniques such as extraction and adsorption could not be taken into account due to a lack of data. However, the highly conjugated systems of 2-cyanopyridine and 2-picolinamide in comparison to the other compounds could give some opportunities.

The difference in volatility between 2-cyanopyridine, 2-picolinamide and the other compounds (methanol, DMC, CO<sub>2</sub>) is very high. Therefore, the separation by distillation is relatively easy.

However, there are some restrictions for this distillation. Under atmospheric pressure, the reboiler temperature is high (about 284°C), so the reboiler cannot be operated with steam. By operating the column below atmospheric pressure the boiling point of the compounds is reduced. Operating the reboiler at 0.5bar results in a temperature of 223.2°C in the reboiler, therefore steam can be used for heating. The condenser in the top operates than still at 51.5°C which is sufficiently high to be cooled by cooling water. Further pressure reduction is a trade-off between costs with respect to reboiler duty and creating (partial) vacuum. Another consideration is that very low pressure may result in a condenser temperature that cannot be achieved by cooling with water. In addition, volumetric vapour flow increases significantly at reduced pressure due to decrease in density.

Secondly, the big temperature gradient over the column may give problems with respect to building material. Azeotropic behaviour between 2-cyanopyridine and 2-picolinamide and one of the other compounds is unknown, but unlikely due to the big differences in boiling points.

Degradation of the agent compounds is not taken into account. Nonetheless, this could be the case because these are already quite complex molecules. However, boiling points are mentioned in literature.

The melting point of 2-picolinamide (110°C) is higher than the boiling point of methanol and DMC. As a result, there may be solid formation if there is 2-picolinamide present on the higher trays. Though, it is probably only present in trace amount and therefore it is probably dissolved.

Thus, distillation is probably the best and safest (with respect to available data) option. It was simulated in UNISIM. Product recovery (2-cyanopyridine and 2-picolinamide) in the bottom was set at 1. Recovery for the top products (Methanol, CO<sub>2</sub> and DMC) was set at 0.99. Minimum reflux ratio could not be determined due to simulation difficulties. However, it is assumed that a reflux of 0.216 is very reasonable at only 6 trays.

Summarizing, S2 is a distillation column which operates below atmospheric pressure. 2-cyanopyridine and 2-picolinamide are the bottom products, while DMC, methanol and CO<sub>2</sub> go over the top. (Column specs: T-2071, 6 Trays, Reflux: 0.216, Feed tray: 5, Pcon = 0.3bar, Preb = 0.5bar, see Appendix F.1)

#### 6.1.2 S3 (Separation of water from the mixture)

According to the article of Bansode et al. [7] all the water is harvested by the dehydrating agent. Thus, there is no water present in the stream after the reactor. S3 is not needed any longer is therefore left out of the PFD.

#### 6.1.3 S4 (DMC-Methanol separation)

In this system, DMC and methanol are separated. The purity of the DMC product is set at 99.8 wt%. The compounds have a significant difference in boiling point, respectively 90°C for DMC and 65°C for methanol. The difficulty here is the formation of an azeotrope, which is located at about 0.85 mole fraction methanol [61]. The main methods described in literature to do this separation are:

- Extractive distillation [62]
- Pressure swing distillation [63]
- Pervaporation [64-67]

The general pros for a form of distillation are its reliability, widely usage and because it is widely known. Cons are the energy usage, especially the two mentioned forms of distillation are extra energy intensive. Pervaporation does have more potential with respect to energy usage, but it is far more experimental. As stated before, literature does show results of DMC-methanol separation by pervaporation, but it is not implemented in industry. Usually, pervaporation is only used to increase quality, not to meet the final spec. Therefore an additional technology is needed to meet the requirements. In addition, distillation technology has the advantage of scaling (the relative decrease in costs when up scaling), membrane technology does not. With a production capacity of 450kton/year this is a major advantage.

The different options with respect to distillation will be further examined.

##### 6.1.3.1 Feed for this separation

The stream that need to be separated contains relatively big amount of DMC, due to the high conversion of methanol and high selectivity towards DMC in the reactor. The exact composition of this stream is shown in Table 10. The total mass flow is 796kmole/h at 88°C and 1.2 bar. The vapour fraction is 0.89.

Table 10: Feed DMC/Methanol separation, trace amounts of other compounds are left out

Compound	Mole fraction
Methanol	0.12
DMC	0.79
CO <sub>2</sub>	0.09

### 6.1.3.2 Possibilities

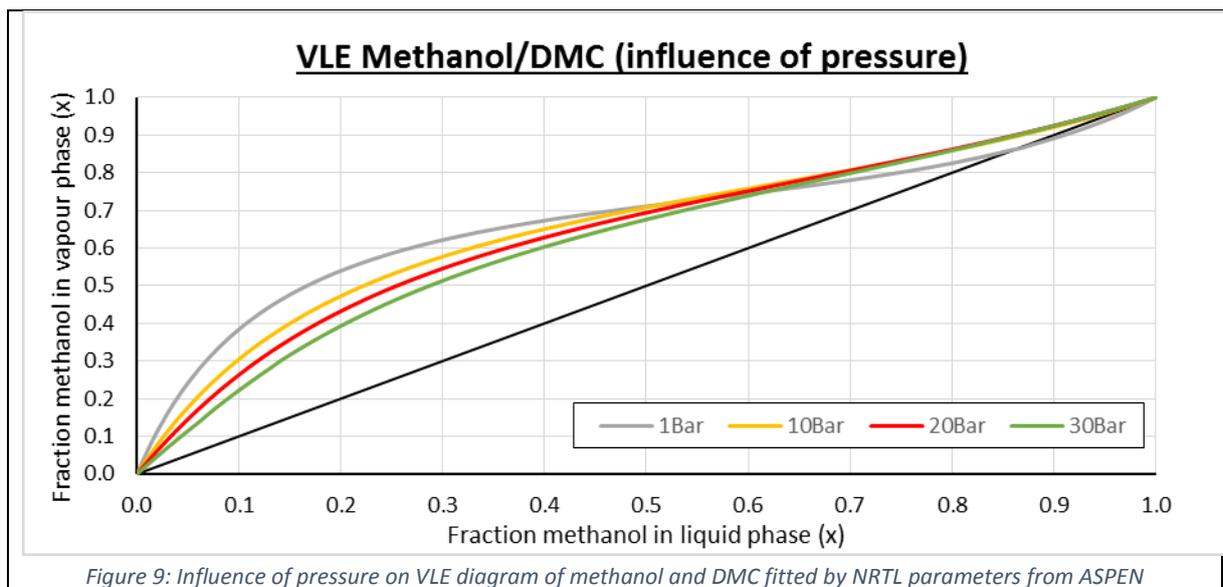
In general there are two possibilities to break the azeotrope by distillation. Either change pressure or use an entrainer. This can completely remove the azeotrope or shift it. The goal is to obtain 99.8 wt% pure DMC as was stated in the scope. The unconverted methanol should be recycled back to the reactor to minimize costs. It should be avoided that this recycle stream contains any DMC, because this will decrease the reactor performance drastically. Therefore, the spec of methanol is set to 99 mole% (with respect to DMC). This is usually defined in the simulator as MeOH/DMC = 99, because there are also other compounds such as CO<sub>2</sub> in the stream. To summarize, the options are:

- Pressurized distillation
- Extractive distillation

#### 6.1.3.2.1 Influence of pressure

The influence of pressure on the azeotrope was determined by constructing VLE graphs with UNISIM by the NRTL parameters from ASPEN, see Figure 9. What can be seen from Figure 9 is that increasing the pressure indeed shifts the azeotrope. However, the azeotrope is still present. In addition, the VLE curve is very close to the equilibrium line near the azeotropic point which makes separation by distillation difficult in this region. Moreover, the effect of increasing the pressure from 10 bar towards 30 bar is not so significant anymore. The azeotropic point shifts to about 0.95 mole% methanol at 10bar and slightly more at 30 bar. So the requested spec cannot be met. Another disadvantage of increasing the pressure is that the boiling points of the compounds increase, and therefore the energy utility of the reboiler increases. Also higher operating pressure is more expensive with respect to CAPEX.

Utilizing pressure to increase purity of the top product can be done. However, the feed of this separation section is mainly vapour (see 6.1.3.1). Therefore, a compressor, which is an expensive piece of equipment, is needed to pressurize this stream. In addition, the stream consists of 9 mole% CO<sub>2</sub>. As a result, liquefying the stream, so a relatively cheap pump can be used to pressurize the stream, is very hard.



#### 6.1.3.2.2 Extractive distillation

In extractive distillation a solvent is added to the mixture. The solvent interacts with mixture and alters the activity coefficients of one or both compounds. As a result, the azeotrope is shifted or even broken. This also depends on the amount of solvent that is added. The goal is to use little solvent as possible, more solvent makes the process more energy intensive. Therefore, the chosen solvent should strongly interact with methanol and/or DMC. In general, with extractive distillation the product can be obtained as pure as requested, just by adding enough solvent.

#### 6.1.3.3 Choice

As stated before, both compounds should be obtained highly pure after the separations. For the bottom product (DMC 99.8 wt%) this gives no problems. However, the methanol purity should be 99 mole% with respect to DMC. Thus, as can be read in 6.1.3.2.1, the influence of pressure is not significant enough to achieve this separation. Therefore, extractive distillation is chosen to separate the DMC methanol mixture.

#### 6.1.3.4 Solvent selection

Effectiveness of extractive distillation for a separation strongly depends on the solvent. The two by far most important criteria for the solvent are:

- It should change the activity coefficients of one of the compounds and thus break the azeotrope. The more the better, which then results in less solvent needed.
- It should not form an azeotrope with one of the compounds (DMC or Methanol)

Another crucial aspect is contact of the solvent with the mixture. For optimal contact, the solvent must travel in the opposite direction of the azeotrope. Thus, in this case the solvent should have a higher boiling point than the azeotropic mixture. As a result, it moves downwards in the column. Usually the solvent enters than at one of the top stages, while the feed enters the column below the solvent.

Additional aspects for a good solvent selection are:

- Safe, preferably non-toxic, non acidic and not flammable
- Preferably big difference between boiling points of compounds in the solvent recovery column (solvent and other compound)
- Melting point that is low enough so no problems occur with solidification and thereby blockage of pipelines etc.
- Low heat of evaporation
- Low cost
- Significant  $\Delta T$  between DMC and solvent (makes separating these easy)

The following compounds were found which could be used as solvent; aniline, ethylene glycol [68], Phenol, [69], 2-ethoxyethanol and 4-methyl-2-pentanone [70]. Phenol was first modelled in UNISIM. It is suitable, however phenol is very toxic. The same is true for aniline. According to Hsu et al. [68] ethylene glycol is not a good entrainer. Thus, an extractive distillation with 2-ethoxyethanol and 4-methyl-2-pentanone were also modelled. Results were poor and requirements could not always be met. Therefore, despite the toxic properties, phenol was chosen as solvent.

VLE data of the modelled solvents was validated (See Appendix F.1).

#### 6.1.3.5 Further options

The feed for this separation step is far from the azeotropic point (see Table 10). Thus, DMC can be obtained highly pure in the bottom of a normal distillation column, because the composition of the feed is at the left of the azeotropic point. The distillate composition can have azeotropic composition at maximum in normal distillation. This gives additional options:

- Extractive distillation
- First normal distillation up to azeotropic composition for the distillate. Followed by extractive distillation

First using a normal distillation column to obtain pure DMC at the bottom and a methanol/DMC mixture with azeotropic composition at the top drastically reduces the flow to a second extractive distillation column. As a result, the amount of solvent that is needed is drastically reduced. However, then 3 columns are needed instead of 2. Though, the extractive (second) and solvent recovery (third) column will be much smaller then. This option is further examined. The columns are optimized one after each other.

#### 6.1.3.6 Distillation up to azeotropic distillate product (T-2072)

The most important spec of this first column is the mass fraction of DMC in the bottom (99.8 wt%). Minimum reflux for this column was determined at 2.52 to meet the DMC spec. As a general rule of thumb the minimum reflux is multiplied with a factor 1.3, this gives an optimum with respect to CAPEX and OPEX. Therefore, the theoretical optimal reflux is 3.28. The minimum amount of stages is 11, with the feed entering at stage 3.

##### 6.1.3.6.1 Distillate composition (T-2072)

The simulator only needs two specs. DMC in the bottom (99.8 wt%) and the reflux which was minimized. So, the composition of the distillate was not locked, but a result from the simulator. The less pure the distillate, the more effort is needed in the following extractive distillation column to separate the mixture. In general, the goal is to minimize the energy consumption of the overall DMC purification section, CAPEX taken into account. Two relevant options occur:

- Let the simulator decide the distillate composition (as in Distillation up to azeotropic distillate product (T-2072) 6.1.3.6).
- Increase the purity of the distillate to near azeotropic composition, while remaining a realistic reflux ratio.

Both options are simulated, results are shown in Table 11. Number 1 is the column defined by the theoretical optimal reflux. In number 2 the purity of the distillate was increased while maintaining a realistic reflux ratio. Amount of trays and the feed tray were kept the same for a fair comparison.

The most important parameters for comparison are the reboiler duty and the recovery of DMC in the bottom. The fraction DMC in the bottom is always 99.8 wt% mass, therefore DMC recovery can be compared by the bottom flows. These are always  $600 \pm 5$  kmol/h (see Table 11), while the distillate flow is always  $196 \pm 5$  kmol/h. Thus changing the distillate composition closer to azeotropic does not make sense (number 2), because the reboiler duty is more than doubled while recovery is not even 2% higher. Condenser duties are ignored, because it is assumed that cooling water is sufficiently available. Thus only pumping cost are required, which are negligible. Option 1 is chosen for this column.

Table 11: Possibilities for T-2072 (simulated by UNISIM), Feed P is equal to P of reboiler, Feed T = 87.97°C, trace amounts of compounds are left out, Pcon =100kPa, Preb =120kPa, Trays: 11, Feed tray: 3, bottom composition: 99.8wt% DMC

Nr.	D (kmole/h)	MeOH	DMC	CO <sub>2</sub>	B (kmole/h)	Reflux ratio	Boil up ratio	Con Duty (kW)	Reb Duty (kW)
1	200.3	0.48	0.16	0.37	596.3	3.28	0.406	6525	2096
2	192.2	0.5	0.12	0.38	604.4	4.63	0.845	8916	4425

#### 6.1.3.6.2 CO<sub>2</sub> content output (T-2072)

The bottom product of T-2072 is 99.8 wt% mass DMC and therefore final product. The distillate stream however needs to be purified further. There is now a very significant amount of CO<sub>2</sub> in the stream (37 mole%), due to the fact that all the CO<sub>2</sub> ends up in the distillate (see Table 12). There are now two possibilities.

Table 12: Composition distillate T-2072, 200.3kmole/h, vapour fraction: 1, P=100kPa

Compound	Mole fraction
Methanol	0.48
DMC	0.16
CO <sub>2</sub>	0.37

- Use the distillate of T-2702 directly as the feedstock for the extractive distillation column (T-2073)
- Remove CO<sub>2</sub> first before extractive distillation

The second option needs an extra separation step thus looks more complex on first sight. Also separating and remixing methanol and CO<sub>2</sub> (they are both recycled) does not make sense. The problem here is that this flash separator is simply unavoidable. Methanol is liquid in the reactor (30bar and 120°C), while CO<sub>2</sub> is gaseous. Pressurizing a mixture of gas and liquid is not possible and therefore CO<sub>2</sub> and methanol need to be separated anyway.

Second option is chosen, CO<sub>2</sub> is removed from the mixture, because it is unavoidable.

#### 6.1.3.6.3 CO<sub>2</sub> separation

High pressure and low temperature are favoured for the separation of methanol and DMC from CO<sub>2</sub>. The distillate stream of T-2072 is cooled followed by a flash vessel (F-2073), results of the streams are shown in Table 13. Table 13 shows that CO<sub>2</sub> is almost eliminated from the liquid stream.

Table 13: Resulting vapour and liquid molar flows of Flash vessel F-2073, P=80kPa, T=20°C

Compound	Vap Mole flow (kmol/h)	Liq Mole flow (kmol/h)
Methanol	12.4	82.8
DMC	4.1	27
CO <sub>2</sub>	73.8	0.15

The vapour stream is not pure enough to recycle. It is assumed that the stream (90.4kmole/h) is still significantly big so that separating is the best option compared to purging. It is compressed to 10bar followed by another flash vessel (F-2074). The vapour stream of this vessel is 98 mole% CO<sub>2</sub>, which is assumed to be pure enough because the stream is not so big. This stream could also be purged. However, it already at 10bar and almost pure CO<sub>2</sub>. It is assumed that the CO<sub>2</sub> feed for the process is at atmospheric pressure. Therefore, it is wise to recycle the stream, because it is easier to compress a stream from 10bar to 30bar than from atmospheric to 30bar.

#### 6.1.3.7 Feed extractive distillation (T-2073)

To summarize the section before; normal distillation followed by a two staged CO<sub>2</sub> separation was executed. The remaining methanol DMC mixture (liquid stream of F-2073 and F-2074) is the feed for the extractive distillation column, composition is shown in Table 14. The feed stream for the extractive distillation is decreased by almost a factor 8.

Table 14: Composition of feed for extractive distillation, preheated, 124.8kmol/h

Compound	Mole fraction
Methanol	0.755
DMC	0.242
CO <sub>2</sub>	0.003

##### 6.1.3.7.1 Extractive distillation (T-2073)

Optimizing an extractive distillation is much more complex than a normal column, because there is an extra variable, the amount of solvent. In addition, the two columns, the extractive and the solvent recovery, must be seen as one unit, because they strongly interact with each other.

It was chosen to minimize the amount of solvent in the first place. Hereby duties of both columns are reduced (when reboil and reflux conditions are not affected). More solvent could possibly reduce the reflux en reboil ratio. However, this will then negatively affect the solvent recovery column.

The minimum reflux was determined thereafter. Following by the scaling down the column while fulfilling the specs and maintaining a reflux of 1.3 x minimum reflux. The result of this column is shown under number 1 in Table 15.

##### 6.1.3.7.2 Optimization (T-2073)

Now some interesting options arise. The feed is liquid and can therefore easily be pressurized. A pressure of 10bar already shifts the azeotropic point significantly as was shown in 6.1.3.2.1. Possibly reflux ratio or solvent amount can be reduced and thereby energy duty. In general CAPEX will not increase so much for equipment suitable for operating at 10bar. OPEX increases due to the increase of boiling temperatures of the compounds. What also should be considered is the steam pressure needed for the reboiler. The temperature in the reboiler should preferably be lower than 250°C, in order to use steam for heating.

Therefore, it was investigated whether operating at 10bar is beneficial. Under number 2 in Table 15 the result of the same column at 10bar is shown. The goal is to reduce the overall energy usage (sum of reboiler duty of extractive and solvent recovery columns). Simply increasing the pressure to 10bar in the extractive column does increase energy duty, thus is undesirable. However, the amount of

solvent can be reduced while maintaining the same reflux ratio (see number 3 in Table 15). Energy duty is already reduced with 288kW compared to number 1. Though, minimum energy usage also depends on the internal flows (reflux and reboil). The amount of solvent was chosen so that the sum of the duties is minimal, the result is shown under number 4 in Table 15. Energy savings of 438kW can be made, plus less solvent is used.

Option number 4 from Table 15 is chosen as T-2073. Though, the final design differs a bit. The feed can be preheated more while remaining liquid, because the pressure is now 10bar instead of 1bar. Hereby reboiler duty is decreased. Also an extra tray is added in the top of the column. This is to minimize the amount of phenol that ends up in the distillate (methanol recycle). Phenol has a melting point of 40°C and therefore can give clogging problems when it accumulates in the process.

Table 15: Possibilities for extractive distillation column (T-2073, simulated by UNISIM), Feed P is equal to P of reboiler, Feed T =68°C, Solvent = Phenol, Distillate comp about: 0.99 methanol 0.01 DMC, Dimensions column: 23 trays, solvent tray: 1, feed tray: 17, Dimensions of solvent recovery column (T-2074): 10 trays, feed tray: 5, atmospheric pressure, Bottom: 0.999 mole% Phenol, Distillate: 99.8 wt% DMC

Nr.	Pcon (bar)	Preb (bar)	S/F	Reflux ratio	Boil up ratio	Reb Duty (kW)	Reb T-2074 (kW)	Sum duties
1	1	1.2	1.04	2.1	1.4	2702	993	3695
2	10	10.2	1.04	1.7	2	3295	763	4058
3	10	10.2	0.43	2.1	3.8	2982	425	3407
4	10	10.2	0.53	1.7	3	2775	482	3257

#### 6.1.3.8 Solvent recovery (T-2074)

The feed for the solvent recovery column is shown in Table 16. There are quite some restrictions for this column so dimensioning is easy. Phenol is high boiling and therefore the bottom product. The DMC top product should be 99.8 wt% pure. The bottom product, phenol, should also be highly pure because it is recycled. Otherwise, DMC enters the extractive column (T-2073) near the top, which makes extractive distillation way more difficult. Therefore the spec for the bottom is set at 0.999 mole fraction phenol. The result of decreasing the spec to 0.99 is an increase of the reflux of the extractive column (T-2073) from 1.8 to 2.6. Moreover, the sum of the reboiler duties increases with about 500kW in this case.

Table 16: Feed composition for solvent recovery column

Compound	Mole fraction
Methanol	0.002
DMC	0.307
Phenol	0.692

The minimum reflux was determined at 0.67. Thus 0.87 is the optimal reflux (multiplying min reflux times 1.3). The column consists of 12 trays, with the feed entering at 5. The reflux is smaller than 0.87, but decreasing the column size results in higher than optimal reflux. Thus, the actual reflux used in this column is a little bit smaller.

A further optimisation opportunity is to integrate the extractive and solvent recovery column into one column. For example, an extractive dividing wall column. However, this is just speculating and not tested.

### 6.1.3.9 Summary

A combination of a normal distillation column followed by an extractive distillation column is used to do the separation. The first column separates the feed (see Table 10) to about azeotropic composition in the top and 99.8 wt% DMC in the bottom. After a cooled and a pressurized flash separation the remaining liquid is fed to the extractive column. In this way, the stream to the extractive distillation column is decreased by almost a factor 8. This was modelled in UNISIM. Phenol is used as the solvent. The extractive distillation column is operated at 10bar. Solvent to feed ratio is about 0.5 (molar based). A summary of the column specs for this separation is given in Table 17. These may slightly differ from the comparisons made in the text, due to additional restrictions (extra preheating of feed, additional tray to prevent phenol in distillate, etc).

Table 17: Summary of specs of the columns used for the separation of DMC-Methanol mixture. Reboiler and condenser are not counted as trays. For detailed temperature, pressure and composition profiles see Appendix F.1

	<b>T-2071 (Near azeotropic)</b>	<b>T-2071 (Extractive)</b>	<b>T-2071 (Solvent recovery)</b>
<b>Trays</b>	11	24	12
<b>Reflux</b>	3.28	1.84	0.829
<b>Feed tray</b>	3	18	5
<b>Solvent tray</b>	-	2	-
<b>Reboiler P (kPa)</b>	120	1020	120
<b>Reb duty (kW)</b>	2132	2588	518

### 6.1.4 S5 (Separation of water from 2-cyanopyridine and 2-picolinamide)

This separation takes place after the regeneration of 2-cyanopyridine. The details of the regeneration are not known yet. In this case the assumption is that the stream after the reactor consists of water, 2-cyanopyridine and 2-picolinamide. In the first separation, water is separated from the other compounds. This could be done with distillation, but it has to be taken into account that 2-cyanopyridine and water may react with each other if the temperature is lowered. The kinetics are hindered by the absence of a catalyst however and thus it can be expected that this is possible. An alternative would be the use of a water permeable membrane. The 2-cyanopyridine needs to be recycled to the first reactor and 2-picolinamide to the regeneration reactor, therefore a high recovery of these compounds is desired.

### 6.1.5 S6 (Separation of 2-cyanopyridine and 2-picolinamide)

In this separator the 2-piridinecarboxamide and 2-cyanopyridine are separated. These are two very similar molecules and thus are hard to separate on the basis of affinity. There is a 70°C difference in boiling points, so distillation could be an option. An alternative can be extraction, the oxygen and amide group of 2-picolinamide might give the opportunity to separate them this way. Hexane is a solvent in which 2-cyanopyridine will dissolve and 2-picolinamide not. The boiling point of hexane is much lower (69°C), so regeneration of the solvent by distillation is not a problem[71]. But then 2-picolinamide is a solid. Maybe a higher boiling alkane is a better option.

## 6.2 Index flowsheet

For the index flowsheet, the previously mentioned separation units are implemented in a flowsheet. Also the heaters, coolers, pumps and compressors are included in the index flowsheet. A detailed process description is given below to summarize the separation step. The index flowsheet can be found in Appendix F.4.

## 6.3 Process description

The process is divided into three parts to make it less complicated:

1. Primary reactor and first separation
2. Regeneration of dehydrating agent
3. Purification of DMC

### 6.3.1 Part one

Methanol, CO<sub>2</sub> and 2-cyanopyridine are fed to the reactor. The feed is assumed to be at 25°C and 1 atm, therefore this needs to be heated and pressurized to the reactor conditions of 30 bar and 120°C. The reactor is a trickle bed reactor (R-2071) in which CO<sub>2</sub> is in the gas phase and the others are in the liquid phase. As a solid phase, the ceria catalyst is present.

The reactor outlet is first sent to a flash separator (F-2071), here the majority of CO<sub>2</sub> goes over the top and almost all pyridine related compounds are collected at the bottom. However, both streams need further purification. There is too much DMC in the gas stream to be recycled immediately and in the bottom almost half of the stream is DMC. The gas is cooled to 20°C and another flash vessel (F-2072) is placed. The resulting gas stream consists of almost pure CO<sub>2</sub> and the liquid is DMC and methanol with some CO<sub>2</sub> dissolved in it.

A low pressure distillation column (T-2071) handles the liquid outlet of the first vessel. In the bottom all the 2-cyanopyridine and 2-picolinamide is recovered and in the top a DMC rich mixture is collected. This mixture is combined with the liquid outlet of F-2072 and sent to part three. The bottom stream of the distillation column will be regenerated in part two.

### 6.3.2 Part two

In this part the dehydrating agent is regenerated. This is a grey area in the process, because very little is known. A reactor (R-2072) converts 2-picolinamide into 2-cyanopyridine, but the kind of reactor, conversion, by-products and operating conditions are unknown.

Assumed is that the reactor outlet consists of water and both previously mentioned compounds. First water is separated as most volatile compound and then 2-cyanopyridine and 2-picolinamide are separated. They are recycled to R-2071 and R-2072 respectively. Although not much is known about this, it plays a crucial role in the economics of the process as presented in chapter 4.

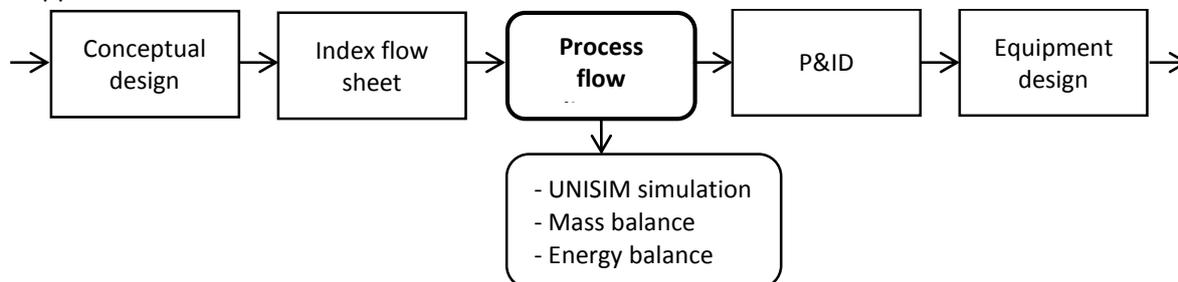
### 6.3.3 Part three

In this section of the plant, DMC is purified. A stream enters the first distillation column (T-2072), where pure DMC is obtained in the bottom and near azeotropic composition of DMC and methanol in the top. This azeotropic mixture is further separated with extractive distillation, but before that two flash vessels (F-2073 and F-2074) will separate the CO<sub>2</sub> that was still left in the stream. The gas stream is pressurized by a compressor (CP-2075) and recycled to the reactor. Both liquid outlets are combined and sent to the extractive distillation column (T-2073). Phenol is used as solvent and collected at the

bottom. An additional distillation column (T-2074) separates DMC and solvent. DMC is combined with the DMC of the first column (T-2072) and the solvent is sent back to the extractive distillation. Methanol is the top product of T-2073 and is recycled to the DMC reactor. This is done by cooling the stream until it liquefies, followed by pressurizing via a pump.

## 7 Process flow diagram

In this chapter the process flow diagram will be given. This is the same as the index flowsheet (Appendix F.4) in the previous chapter, but now the mass and energy balances are made over the process. This is done by simulating the process in UNISIM and the complete mass balance can be found in Appendix G.1.



### 7.1 UNISIM simulation

In UNISIM the simulations of the process has been carried out. The fluid package is chosen based on the validation of UNISIM results for VLE data with literature. NRTL will be used to describe the liquid phase and Redlich-Kwong is chosen for the vapour phase (see Appendix F.1). Data for DMC, 2-cyanopyridine and 2-picolinamide are not available in UNISIM. For DMC the interaction parameters are taken from software package APSEN and the DECHEMA data series, but 2-cyanopyridine and 2-picolinamide are not and interaction parameters are estimated by UNISIM.

### 7.2 Mass balance

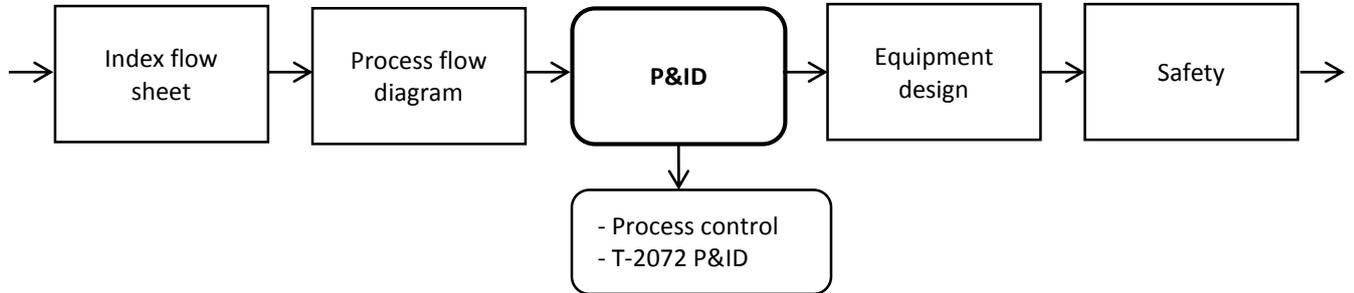
The simulation results in a mass balance in which the temperature, pressure, vapour fraction, flows and composition are given. The stream numbers are consistent with the process flow diagram. In the PFD, the number change when a unit is placed that changes the composition. In UNISIM however, also after a unit that changes pressure or temperature a new stream number has to be given. For example stream 1 is than split into 1a and 1b. In Appendix G.1 the mass balance with the characteristics for the streams is shown.

### 7.3 Energy balance

From the simulation also an energy balance is extracted. The energy flows are added as a row to the mass balance, see Appendix G.1.

## 8 P&ID

In this chapter a piping and instrumentation diagram (P&ID) is made. The first step is the control set up and is designed for the whole process. A P&ID is in too much detail to made for the complete process. Therefore only for T-2072 a detailed P&ID is made. This uses the HAZOP made in chapter 10.4.



### 8.1 Process control

In this section the required process control set up is designed. First the control measures for different unit operations are design and then this is done for the whole process. The process is split in three parts; main reactor and flash separators (F-2071, F-2072), regeneration and DMC purification. To do this in a systematic manner, a work diagram is developed and this is shown in Figure 10.

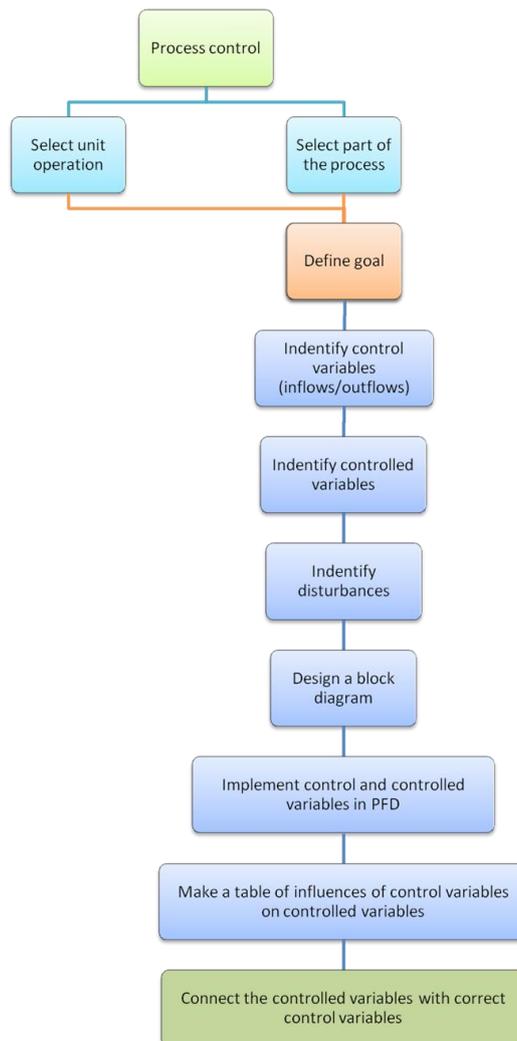


Figure 10: Work diagram for process control

### 8.1.1 Unit operations

For the flash vessels, heaters cooler and distillations columns the control set up is designed. The final design is shown here, the detailed derivation of it can be found in Appendix H.1.

#### 8.1.1.1 Flash vessel

The control set up for the flash vessels (F-2071, F-2072, F2073 and F-2074) is shown Figure 11.

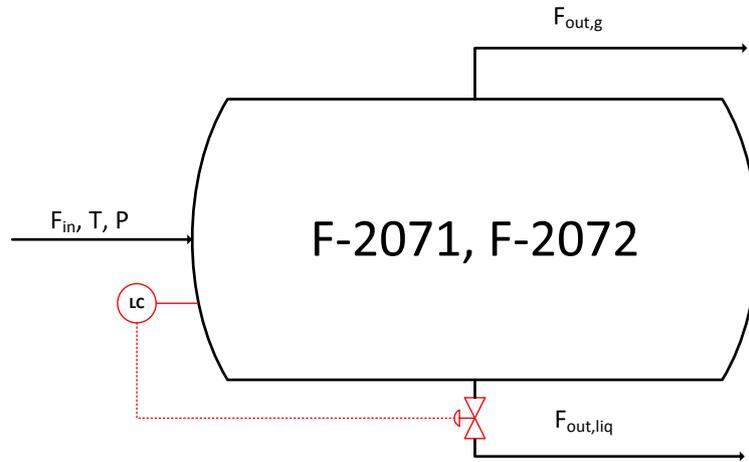


Figure 11: Control set up for a flash vessel

#### 8.1.1.2 Heater

In Figure 12 the control set up for the heaters is shown. This is valid for all the heaters (H-2071, H-2072, H-2073, H2074, H-2075, H-2076 and H-2078).

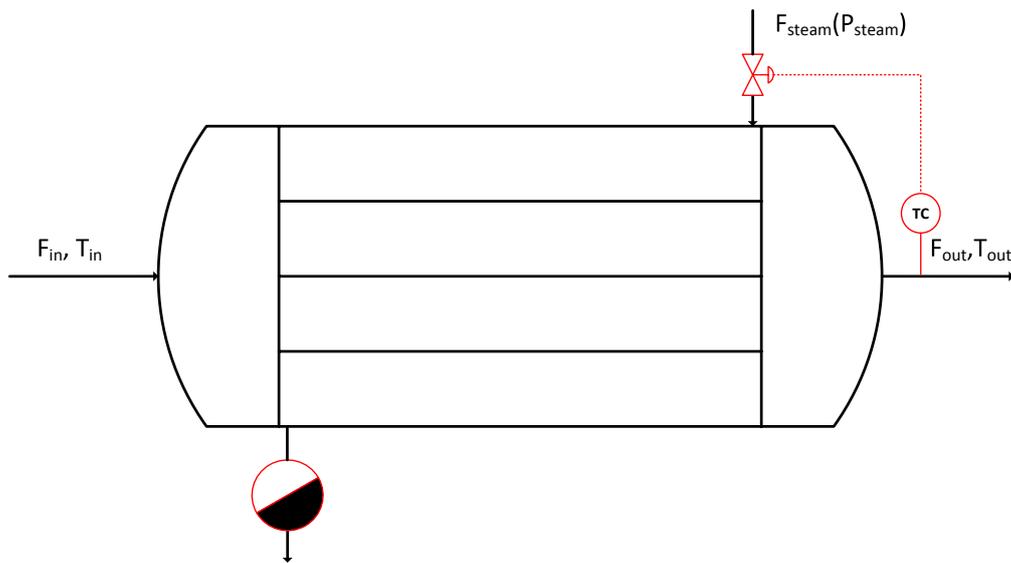


Figure 12: Control set up for a heater

#### 8.1.1.3 Cooler

For the coolers (CL-2071 until CL-20710, reboilers and condensers) a similar control system as for the heater is designed. This is shown in Figure 13.

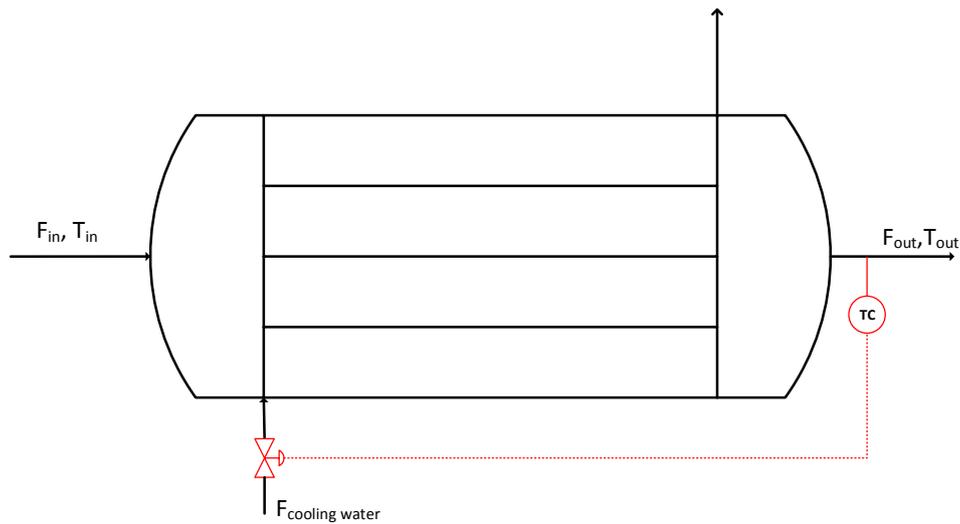


Figure 13: Control set up for a cooler

#### 8.1.1.4 Distillation column

Multiple distillation columns are present in the process, for every column a process control set up is designed. Figure 14 gives the first two distillation columns, as they have the same top product phase and goals. The complete process control set up for the extractive distillation column with solvent regeneration is shown in Figure 15.

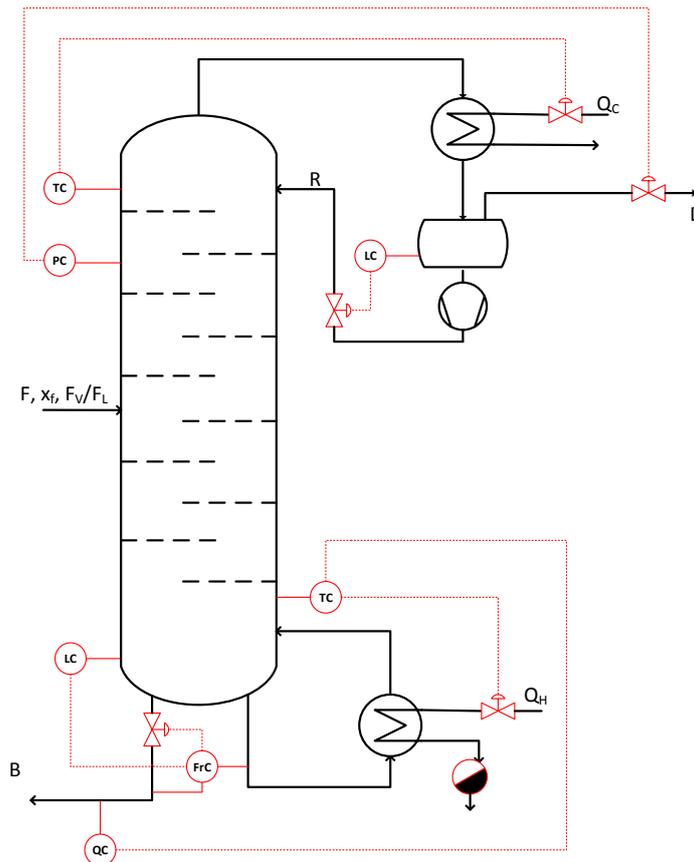


Figure 14: Control scheme of the distillation column T-2072 to obtain pure DMC and low pressure distillation column (T-2071)

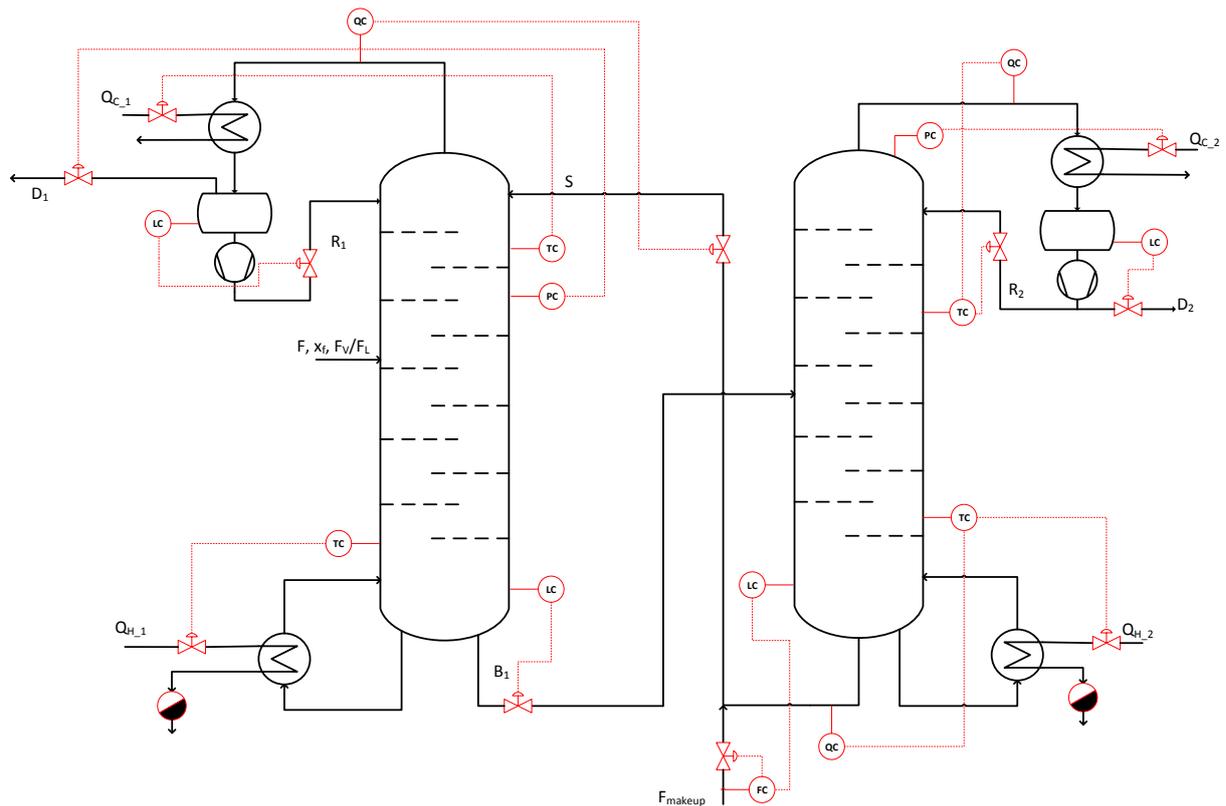


Figure 15: Process control set up for the extractive distillation column and solvent regeneration column

### 8.1.2 Process

Only designing a control scheme for the different unit operations will not be sufficient. In this section the other addition process control set up is made. To make it less complicated, the process is divided into three parts:

- 1) Reactor and first two flash vessels
- 2) Regeneration of dehydrating agent
- 3) Purification of DMC

Only for the purification of DMC, no additional process control equipment is necessary. For the first and second part however, additional process control set up is required.

The process control set up for these parts are given in respectively Figure 16 and Figure 17. A detailed analysis is given in Appendix H.1.



## 8.2 Piping and instrumentation diagram

In the previous chapter the process control set up of the complete plant is designed. This already a start of the piping and instrumentation diagram (P&ID). To make the P&ID complete, all the safety equipment has to be installed, this is done in combination with the HAZOP (Chapter 10.4). Only one major equipment has to be chosen to make a detailed P&ID. Here is chosen for the distillation column which separates methanol and DMC (T-2072) to obtain pure DMC and the azeotropic mixture.

Some information about the P&ID:

- All level controllers have a low and high alarm. This is not specifically shown in the diagram
- Shut down valves are annotated with 'SDV'
- Shut down valves and control valves are linked to the indicators on which they react

The complete P&ID can be found in Figure 18 on page 48.

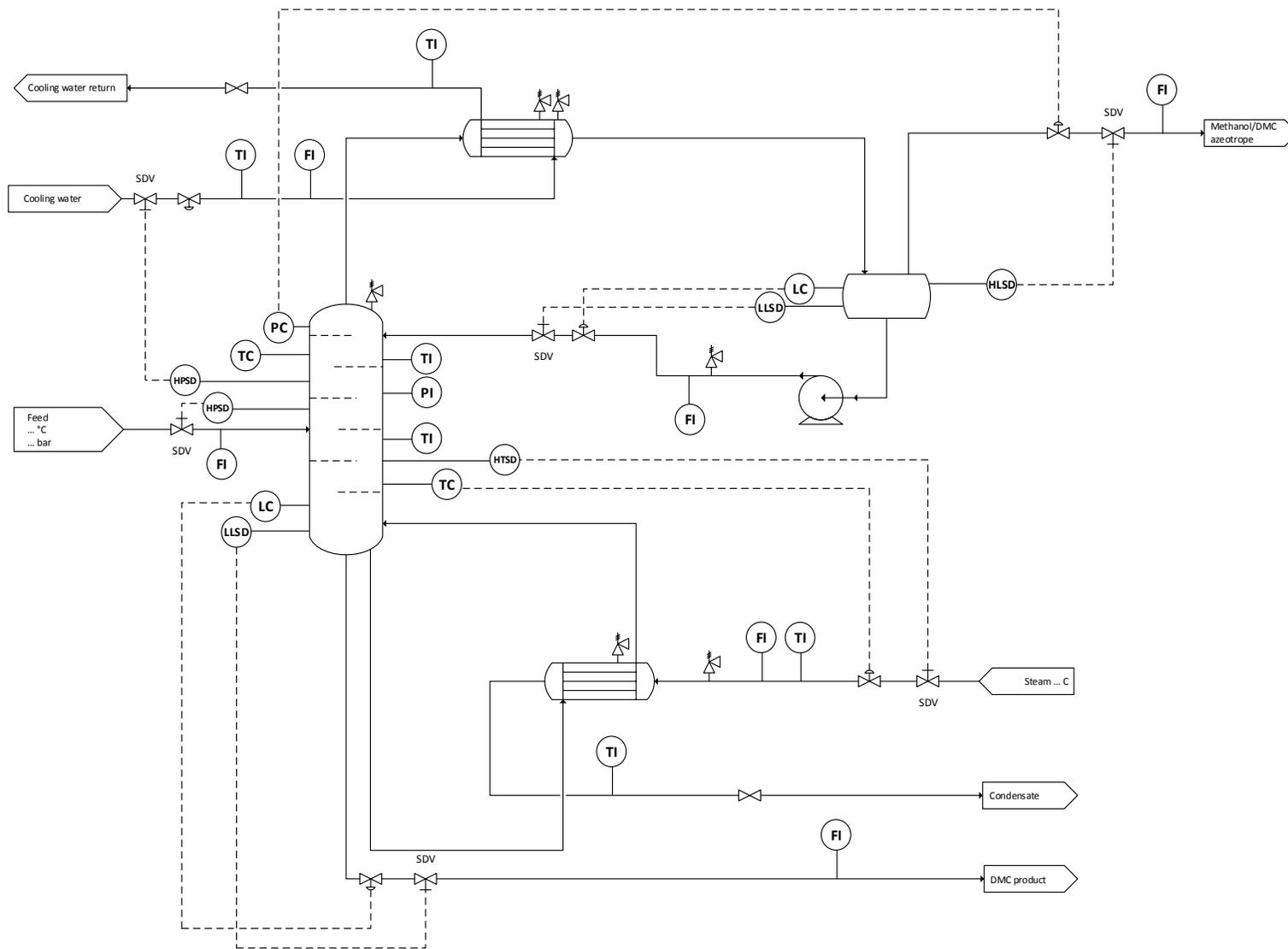
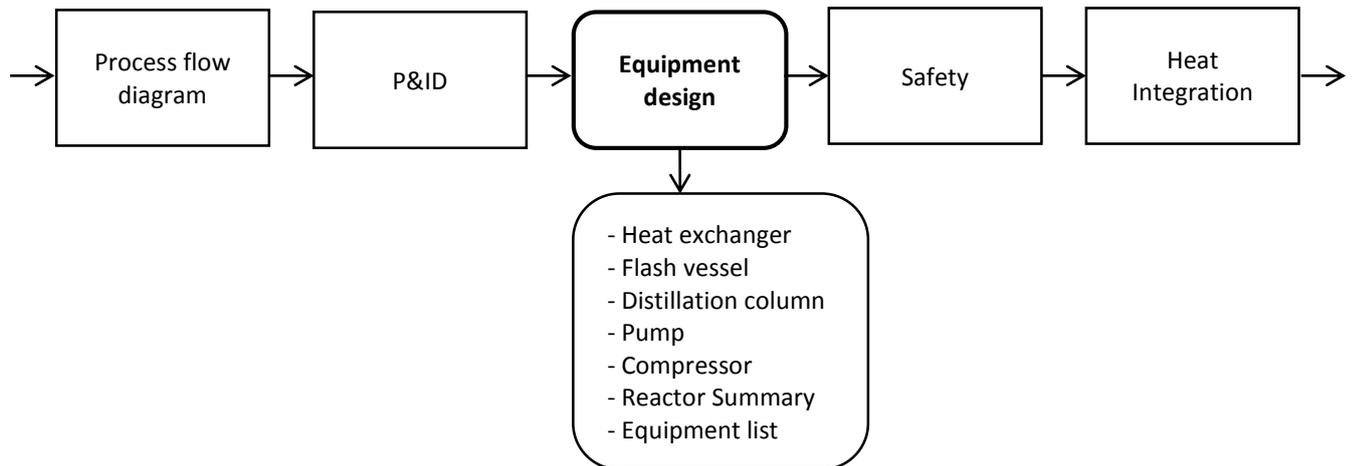


Figure 18: Piping and instrumentation diagram for T-2072

## 9 Equipment design

The process flow diagram is complete and that means all necessary equipment is known. In this chapter this equipment is designed. The detail of design is different for every different piece of equipment. Eventually the goal of the design is to have enough data to estimate the capital costs of the equipment. Therefore, the level of detail is equivalent to the parameters needed for the economic evaluation. The economic evaluation is covered in chapter 12.

In this chapter only a summary of the equipment is given, the detailed design can be found in Appendix I.1.



### 9.1 Heat exchanger

Heat exchangers are used to heat up streams or cool down streams to a desired temperature. As heat integration between process streams is not evaluated, only heaters and coolers are in place. Also interstage cooling in compressors are treated as heat exchangers. Another class of heat exchangers, which are also included in this paragraph are reboilers and condensers.

To summarize, all equipment that has the goal to exchange heat is designed in this paragraph.

Table 18 gives an overview of all heat exchangers with the required parameters for the economic evaluation. A detail design is given in Appendix I.1.1.

Table 18: Summary of heat exchangers present in the process

Name	Type	Tin [C]	Tout [C]	Pshell [bar]	Duty [kW]	A [m <sup>2</sup> ]	Material [shell/tube]	Medium	Flow [kg/s]	Tube length [ft]
CL-2071	U-tube	120	20	30.0	-4.03E+03	6.48E+02	CS/CS	Chilled water	95.87	20
CL-20710	Double-pipe	89	20	1.0	-3.25E+01	4.72E+00	CS/CS	Cooling water	0.52	20
CL-2072	U-tube	52	20	1.0	-1.21E+03	1.84E+02	CS/CS	Chilled water	28.79	20
CL-2073	U-tube	137	85	10.0	-9.38E+02	2.23E+01	CS/CS	Cooling water	14.96	20
CL-2074a	Double-pipe	120	45	2.4	-7.77E+01	1.39E+01	CS/CS	Cooling water	1.24	20
CL-2074b	Double-pipe	122	60	5.0	-6.59E+01	8.81E+00	CS/CS	Cooling water	1.05	20
CL-2074c	U-tube	133	20	10.2	-2.76E+02	4.11E+01	CS/CS	Chilled water	6.57	20
CL-2075	U-tube	223	120	1.4	-3.42E+03	8.98E+01	CS/CS	Cooling water	54.55	20
CL-2076a	U-tube	128	40	3.0	-6.15E+02	1.79E+02	CS/CS	Cooling water	9.81	20
CL-2076b	U-tube	146	40	8.3	-7.55E+02	1.89E+02	CS/CS	Cooling water	12.04	20
CL-2076c	U-tube	144	95	23.5	-3.70E+02	3.11E+01	CS/CS	Cooling water	5.90	20
CL-2077	U-tube	124	65	0.7	-4.59E+02	2.99E+01	CS/CS	Cooling water	7.32	20
CL-2078	U-tube	95	20	1.2	-7.56E+02	1.62E+02	CS/CS	Cooling water	12.06	20
CL-2079	Double-pipe	245	160	10.0	-4.55E+02	9.33E+00	SS/SS	Cooling water	7.26	20
H-2071	U-tube	46	147	11.4	3.50E+03	2.97E+02	CS/CS	Steam medium	1.75	20
H-2072	U-tube	31	150	11.4	5.64E+03	9.29E+01	CS/CS	Steam medium	2.82	20
H-2073	U-tube	123	150	11.4	8.74E+02	2.44E+01	CS/CS	Steam medium	0.44	20
H-2074	U-tube	117	150	11.4	1.69E+03	4.49E+01	CS/CS	Steam medium	0.85	20
H-2075	Double-pipe	20	50	4.5	1.20E+02	1.43E+00	CS/CS	Steam low	0.06	20
H-2076	Double-pipe	21	125	4.5	4.10E+02	9.03E+00	CS/CS	Steam low	0.19	20
H-2078	U-tube	118	150	11.4	3.68E+03	9.85E+01	CS/CS	Steam medium	1.84	20
T-2071 Con	U-tube	51	50	0.3	-1.28E+03	1.87E+02	CS/CS	Cooling water	20.42	20
T-2071 Reb	U-tube	223	224	32.0	3.88E+03	1.68E+01	CS/CS	Steam high	2.19	20
T-2072 Con	U-tube	52	51	1.0	-6.50E+03	8.64E+02	CS/CS	Cooling water	103.68	20
T-2072 Reb	U-tube	95	96	4.5	2.13E+03	4.10E+01	CS/CS	Steam low	1.00	20
T-2073 Con	Double-pipe	137	136	10.0	-1.41E+03	1.68E+01	CS/CS	Cooling water	22.49	20
T-2073 Reb	U-tube	245	246	42.0	2.59E+03	3.27E+02	CS/SS	Steam very high	1.53	20
T-2074 Con	Double-pipe	89	88	1.0	-4.71E+02	1.09E+01	CS/CS	Cooling water	7.51	20
T-2074 Reb	Double-pipe	188	189	32.0	5.18E+02	1.06E+01	CS/SS	Steam high	0.29	20

For the operational expenses, the utilities need to be known. In this case the amount of heating and cooling media. The total requirement for every utility is listed in Table 19.

Table 19: Total utilities needed for the heat exchangers

Utilities	
Chilled water	131.22 kg/s
Cooling water	280.83 kg/s
Steam low	1.25 kg/s
Steam medium	7.70 kg/s
Steam high	2.48 kg/s
Steam very high	1.53 kg/s

## 9.2 Flash vessel

Four flash vessels are present in the process. In general there are two types of flash vessels; horizontal and vertical. Two of each are selected for the process. All parameters for the economic evaluation can be found in Table 20. Appendix I.1.2. gives a detailed equipment design. Flash vessels do not need a utility.

Table 20: Summary of flash vessels in the process

Name	Type	Po [bar]	To [°C]	Length [m]	Diameter [m]	Demister pad?
F-2071	Vertical	30.00	120.00	7.86	3.99	N
F-2072	Vertical	29.80	20.00	3.79	1.34	Y
F-2073	Horizontal	0.80	20.00	3.00	1.00	Y
F-2074	Horizontal	10.00	20.00	1.80	0.60	N

### 9.3 Distillation column

Distillation columns are designed in little detail, as been carried out in Appendix I.1.3. A simple estimation of the height and diameter is carried out. The number of theoretical equilibrium stages and vapour flow rate are adapted from the UNISIM simulation, which are the basis for the height and diameter respectively. In Table 21 a summary of the important parameters for the distillation columns are given. The utilities are in the reboiler and condenser, but this is already covered by the heat exchanger section.

Table 21: Overview of distillation columns present in the process

Number	Internal	Diameter [m]	Height [m]	To [°C]	Po [bar]	NT	Type	Material	Packing	Packing length [m]	# Distributors
<b>T-2071</b>	Packing	3.41	6.86	223.2	0.5	-	-	-	Structured	2.86	2
<b>T-2072</b>	Plate	2.72	12.00	95.5	1.2	16	Sieve	CS	-	-	-
<b>T-2703</b>	Plate	0.86	21.50	224.9	10.2	35	Sieve	SS316	-	-	-
<b>T-2074</b>	Plate	0.85	13.00	187.7	1.2	18	Sieve	SS316	-	-	-

### 9.4 Pump

A summary of the pumps is given in Table 22. In total there are five reciprocating plunger pumps, three gear pumps and one centrifugal pump. P-2076 is not present in the list, because it is located in the regeneration section and this part is not considered in this project. The pumps are design in detail in Appendix I.1.4.

Table 22: Summary of the pumps present in the process

Number	Flow rate [m <sup>3</sup> /s]	Head [m]	Pump type	Power [Hp]	η <sub>P</sub>	η <sub>M</sub>	Material
<b>P-2071</b>	1.42E-02	378.70	Plunger	68.57	0.90	0.90	Cast iron
<b>P-2072</b>	1.35E-05	277.40	Plunger	1.25	0.90	0.80	Cast iron
<b>P-2073</b>	1.53E-03	106.83	Plunger	2.66	0.90	0.82	Plunger
<b>P-2074</b>	1.19E-03	286.16	Plunger	4.31	0.90	0.84	Cast iron
<b>P-2075</b>	6.88E-04	1.92	Gear	1.00	0.80	0.65	Cast iron
<b>P-2077</b>	2.11E-02	300.18	E	133.40	0.67	0.91	Cast iron
<b>P-2078</b>	2.33E-02	8.88	Gear	4.20	0.80	0.84	Cast iron
<b>P-2079</b>	2.17E-04	4.43	Plunger	1.25	0.90	0.80	Cast iron
<b>P-20710</b>	1.89E-03	100.40	Gear	3.43	0.80	0.83	SS

Electricity is used to drive the pumps. The total requirements of utilities can be found in Table 23.

Table 23: Total required utility for the pumps

Utilities	
<b>Electricity</b>	164.11 kW

### 9.5 Compressor

In the process some high pressure unit operations are present and gaseous compounds as CO<sub>2</sub> need to be compressed. In total five compressors are needed. The result of the design (Appendix I.1.5) is summarized in Table 24. Three centrifugal compressors and one reciprocating compressor are selected and also one centrifugal blower is needed. Table 25 gives the utilities for the compressors.

Table 24: Summary of the compressors in the process

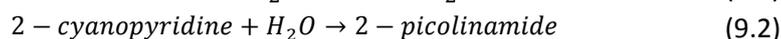
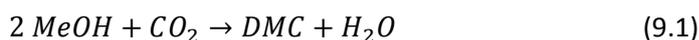
Number	Type		Gas flow [m <sup>3</sup> /s]	Pin [bar]	Pout [bar]	Power [Hp]	Material	Motor
CP-2071	Compressor	Centrifugal	4.28	1.00	30.20	4084.20	Carbon steel	Electric
CP-2072	Blower	Centrifugal	0.39	29.80	30.20	31.01	Cast iron	-
CP-2073	Compressor	Centrifugal	15.80	0.30	1.20	1513.36	Carbon steel	Electric
CP-2074	Compressor	Centrifugal	0.76	0.80	10.20	392.63	Carbon steel	Electric
CP-2075	Compressor	Reciprocating	0.05	10.00	30.20	101.40	Carbon steel	Electric

Table 25: The sum of utility requirements for the compressors

Utilities	
Electricity	4565.62 kW

## 9.6 Reactor

The methanol/CO<sub>2</sub> reactor design is described here; the detailed design is described in Appendix I.1.6. In this reactor methanol and CO<sub>2</sub> are used to react to DMC and water. Water reacts with 2-cyanopyridine to push the equilibrium of the previous reaction to the DMC side.



The reactor uses an excess of CO<sub>2</sub> compared to the liquid methanol and 2-cyanopyridine, also a solid catalyst is used. The volume flow of the gas phase is much higher than the volume flow of the liquid phase and the reactor is in three phases, thus a trickle bed reactor is chosen. The reactor will be multitubular because otherwise the heat cannot be removed properly. These tubes will be divided in multiple shells because of a maximum shell diameter of 1.52m for practical reasons[72]. It is assumed that the catalyst must be replaced every month, therefore extra shells are needed. An overview of the reactor and its results is shown in Table 27. The reaction is not limited by mass transfer. Thus counter current operation does not have an advantage. Therefore, it was chosen to operate the reactor co current, because it is easier to operate.

The main constraints on the reactor system where that the temperature of the reactor could not be above 130°C because of side product formation. Secondly the conversion had to be over 92.4% (the value Bansode et al. reached [7]) and the production had to be higher than 450kton DMC/a to reach the goal production of the plant. The conversion is chosen because this is the value that was used in the process. These constraints are shown in Table 26.

Table 26: Reactor constraints

Parameter	Value
Reactor temperature	<130°C
C <sub>methanol</sub> /C <sub>2-cyanopyridine</sub>	2
Mol CO <sub>2</sub> in/mol methanol in	2.5
DMC production	450 kton/year
Methanol Conversion	>92.4%
Gas velocity	<0.6 m/s
Liquid mass velocity	<12 kg/m <sup>2</sup> /s

To reach these constraints the tube diameter, reactor tube length and tube amount of tubes were varied in that order. The tube diameter was varied to reach the desired temperature effect, the tube length to reach the desired conversion and the amount of tubes to reach the desired production. Virtually infinite options are possible, but this was the most feasible found. Other options are shown in Appendix I.1.6. Table 27 gives the design parameters for the DMC reactor.

Table 27: Reactor properties

Parameter	Value
Inlet superficial gas velocity	0.2 m/s
Inlet superficial liquid velocity	0.0072 m/s
Cooling temperature/Inlet temperature	120°C
Void fraction in the reactor	0.5
Reactor tube diameter	0.065 m
Reactor tube length	14.5 m
Amount of tubes for reaction	1575
Amount of tubes needed	2363
Particle diameter in the reactor	0.005 m
Maximum temperature in the reactor	129.6°C
Conversion over the reactor	92.7%
Production	461 kton DMC/year
Pressure drop	$2 \cdot 10^4$ Pa
Amount of shells for reaction	8
Amount of shells needed	10

## 9.7 Summary

In this chapter a design is made for all equipment in the process. These are 1 reactor, 29 heat exchangers, 4 flash vessels, 4 distillation columns, 9 pumps and 5 compressors. The design parameters will be used in chapter 12 for the economic evaluation.

Next to the equipment, also the required utilities are calculated. The complete utilities are listed in Table 28.

Table 28: Utility requirements for the complete process

Utilities	
<b>Chilled water</b>	131.22 kg/s
<b>Cooling water</b>	430.83 kg/s
<b>Steam low</b>	1.25 kg/s
<b>Steam medium</b>	7.70 kg/s
<b>Steam high</b>	2.48 kg/s
<b>Steam very high</b>	1.53 kg/s
<b>Electricity</b>	4729.73 kW

## 9.8 Equipment list

Compressor							
Name	Stream #	P <sub>in</sub> (bar)	P <sub>out</sub> (bar)	ΦV (m3/s)	Power (Hp)	Type	Description
CP-2071	1	1.0	30.2	4.28	4084.20	Centrifugal	Pressurizing CO <sub>2</sub> feed, stagewise cooling
CP-2072	12	29.8	30.2	0.39	30.01	Blower	Pressurizing CO <sub>2</sub> recycle (1)
CP-2073	14	0.3	1.2	15.80	1513.36	Centrifugal	Pressurizing after low pressure distillation
CP-2074	19	0.8	10.2	0.76	392.63	Centrifugal	Pressurize for better flash separation
CP-2075	22	10.0	30.2	0.05	101.40	Reciprocating	Pressurizing CO <sub>2</sub> recycle (2)
<b>Total:</b>	<b>5</b>	<b>compressors</b>			<b>6121.60</b>		

Pump							
Name	Stream #	P <sub>in</sub> (bar)	P <sub>out</sub> (bar)	ΦV (m3/s)	Power (Hp)	Material	Description
P-2071	2	1.0	30.2	1.42E-02	68.57	Carbon Steel	Pressurizing methanol feed
P-2072	3	1.0	30.2	1.35E-05	1.25	Carbon steel	Pressurize 2-cyanopyridine feed
P-2073	20	0.8	10.4	1.53E-03	2.66	Carbon steel	Pressurize for extractive distillation column
P-2074	27	9.8	30.2	1.19E-03	4.31	Carbon steel	Pressurizing recycle of methanol
P-2075	28	0.8	1.0	6.88E-04	1.00	Cast iron	Pressurize for DMC storage
P-2077	35	1.2	30.2	2.11E-02	133.40	Cast iron	Pressurizing 2-cyanopyridine recycle
P-2078	15	0.5	1.4	2.33E-02	4.20	Cast iron	Pressurize for agent regeneration
P-2079	21	10.0	10.4	2.17E-04	1.25	Carbon steel	Pressurizing for extractive distillation column
P-20710	30	1.2	10.2	1.89E-03	3.43	SS	Pressurizing for agent regeneration
<b>Total:</b>	<b>9</b>	<b>pumps</b>			<b>220.07</b>		

Reactor							
Name	Stream # in	Stream # out	P (bar)	T (°C)	Phase	Type	Description
R-2071	4, 5, 6	7	30	120	G/L/S	Trickle bed	DMC synthesis reactor
R-2072	31	32	Unknown	Unknown	Unknown	Unknown	Regeneration reactor
<b>Total:</b>	<b>2</b>	<b>reactors</b>					

Flash vessel							
Name	Length (m)	Diameter (m)	P (bar)	T <sub>feed</sub> (°C)	Demister pad	Orientation	Description
F-2071	7.86	3.99	30.0	120.0	N	Vertical	First G/L separation
F-2072	3.79	1.34	29.8	20.0	Y	Vertical	Purifying CO <sub>2</sub> for recycle
F-2073	3.00	1.00	0.8	20.0	Y	Horizontal	Separating CO <sub>2</sub> in two steps with F-2074
F-2074	1.80	0.60	10.0	20.0	N	Horizontal	Separating CO <sub>2</sub> in two steps with F-2073
<b>Total:</b>	<b>4</b>	<b>Flash vessels</b>					

Distillation column							
Name	Length (m)	Diameter (m)	Internal	T <sub>reb</sub> (°C)	P <sub>max</sub>	Number of trays	Description
T-2071	6.86	3.41	Packing	223.2	0.5	-	Low pressure separation to purify DHA
T-2072	12.00	2.72	Plate	95.5	1.2	16	Primary DMC/MeOH distillation column
T-2073	21.50	0.86	Plate	224.9	10.2	35	Extractive distillation column
T-2074	13.00	0.85	Plate	187.7	1.2	18	Solvent regeneration column
<b>Total:</b>	<b>4</b>	<b>Distillation columns</b>					

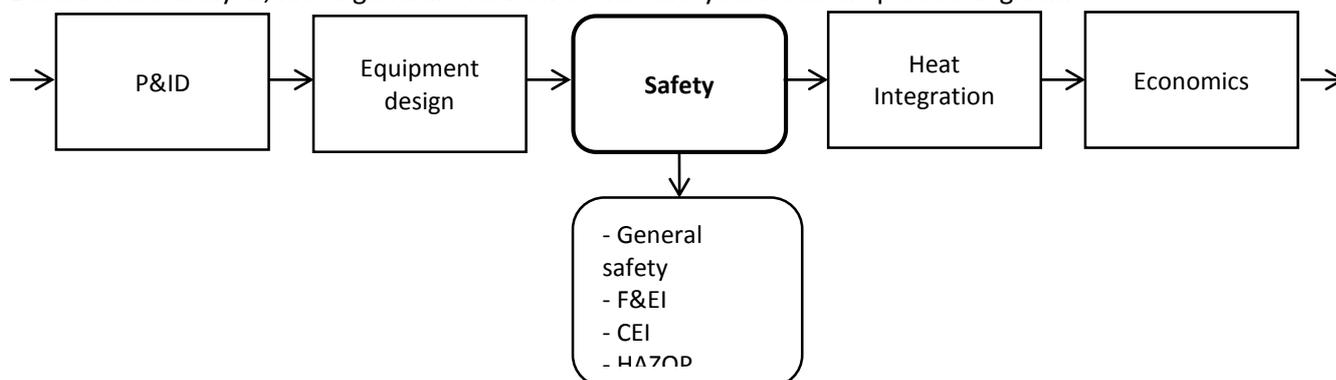
Coolers							
Name	Stream #	T <sub>in</sub> (°C)	T <sub>out</sub> (°C)	P <sub>shell</sub> (bar)	Duty (kW)	Area (m2)	Description
CL-2071	9	120.0	20.0	30.0	-4.03E+03	648.39	Cooling between flash vessels F-2071 and F-2072
CL-20710	28	89.0	20.0	1.0	-3.25E+01	4.72	Cooling DMC product to storage
CL-2072	18	52.0	20.0	1.0	-1.21E+03	184.36	Cooling stream before F-2073
CL-2073	27	137.0	85.0	10.0	-9.38E+02	22.32	Liquefying methanol recycle
CL-2074a	19	120.0	45.0	2.4	-7.77E+01	13.89	Interstage cooling CP-2074
CL-2074b	19	122.0	60.0	5.0	-6.59E+01	8.81	Interstage cooling CP-2074
CL-2074c	19	133.0	20.0	10.2	-2.76E+02	41.10	Interstage cooling CP-2074
CL-2075	15	223.0	120.0	1.4	-3.42E+03	89.79	Cooling T-2072 bottom stream for regeneration
CL-2076a	1	128.0	40.0	3.0	-6.15E+02	178.61	Interstage cooling CP-2071
CL-2076b	1	146.0	40.0	8.3	-7.55E+02	188.65	Interstage cooling CP-2071
CL-2076c	1	144.0	95.0	23.5	-3.70E+02	31.12	Interstage cooling CP-2071
CL-2077	14	124.0	65.0	0.7	-4.59E+02	29.94	Cooling after CP-2077
CL-2078	17	95.0	20.0	1.2	-7.56E+02	162.08	Cooling DMC product to storage
CL-2079	26	245.0	160.0	10.0	-4.55E+02	9.33	Cooling bottom stream of extractive distillation
<b>Total:</b>	<b>14</b>	<b>Coolers</b>			<b>-1.35E+04</b>		

Heater							
Name	Stream #	T <sub>in</sub> (°C)	T <sub>out</sub> (°C)	Pshell (bar)	Duty (kW)	Area (m2)	Description
H-2071	4	46.0	147.0	11.4	3.50E+03	297.42	CO2 heater before R1
H-2072	5	31.0	150.0	11.4	5.64E+03	92.94	Methanol heater before R1
H-2073	6	123.0	150.0	11.4	8.74E+02	24.41	2-cyanopyridine heater before R1
H-2074	8	117.0	150.0	11.4	1.69E+03	44.88	Heater to keep 2-picolinamide liquid
H-2075	10	20.0	50.0	4.5	1.20E+02	1.43	DMC/MeOH heater after F-2071
H-2076	23	21.0	125.0	4.5	4.10E+02	9.03	Extractive distillation feed heater
H-2078	8	118.0	150.0	11.4	3.68E+03	98.53	Heater to keep 2-picolinamide liquid
<b>Total:</b>	<b>7</b>	<b>Heaters</b>			<b>1.59E+04</b>		
Reboiler							
Name	Stream #	T <sub>in</sub> (°C)	T <sub>out</sub> (°C)	Pshell (bar)	Duty (kW)	Area (m2)	Description
T-2071 reb	4	223	224	32	3.88E+03	16.78	Low pressure separation to purify DHA
T-2072 reb	5	95	96	4.5	2.13E+03	41.00	Primary DMC/MeOH distillation column
T-2073 reb	6	245	246	42	2.59E+03	326.74	Extractive distillation column
T-2074 reb	8	188	189	32	5.18E+02	10.58	Solvent regeneration column
<b>Total:</b>	<b>4</b>	<b>Reboilers</b>			<b>9.12E+03</b>		
Condenser							
Name	Stream #	T <sub>in</sub> (°C)	T <sub>out</sub> (°C)	Pshell (bar)	Duty (kW)	Area (m2)	Description
T-2071 con	4	51.0	50.0	0.3	-1.28E+03	187.25	Low pressure separation to purify DHA
T-2072 con	5	52.0	51.0	1.0	-6.50E+03	864.45	Primary DMC/MeOH distillation column
T-2073 con	6	137.0	136.0	10.0	-1.41E+03	16.78	Extractive distillation column
T-2074 con	8	89.0	88.0	1.0	-4.71E+02	10.93	Solvent regeneration column
<b>Total:</b>	<b>4</b>	<b>Condensers</b>			<b>-9.66E+03</b>		

## 10 Safety

Safety is always an important factor at a chemical facility. In this chapter, some parts of the safety considerations during the design of a process are considered. To apply a full safety analysis over the complete plant is too much for this project, therefore the safety is considered for a small part of the plant. The fire and explosion index is made for the important equipment, a chemical exposure index is made for one single stream and a HAZOP is carried out for the second distillation column, which separates DMC and methanol to the azeotropic point.

Before these analysis, first a general overview of the safety issues in the process is given.



### 10.1 General safety

For the safety it is important to first know the compounds in the process:

Table 29: Materials in the system

	Flash point	F&EI material factor
<b>Methanol</b>	12°C	16
<b>Carbon dioxide</b>	-	-
<b>Dimethyl carbonate</b>	17°C	16
<b>Phenol</b>	79°C	10
<b>2-Cyanopyridine</b>	89°C	Not known
<b>Picolinamide (2-pyridinecarboxamide)</b>	Not known	Not known

In our process the methanol involved is the most dangerous for fire hazards. Since it is used in liquid form above atmospheric boiling point under pressure it has an explosion risk in case of a fire. The methanol also releases a lot of heat when burned ( $\Delta H_c = 710$  kJ/mol) and the flash point is very low at 12°C [59]. DMC has about the same flash point at 17°C [60]. Phenol also has a high enthalpy of combustion at 3058 kJ/mol, but its flash point is much higher at 79°C [73]. The same goes for the dehydrating agents. The flash point of 2-cyanopyridine is 89.0°C and while the flash point of 2-picolinamide is unknown, it can be expected to be higher than that of 2-cyanopyridine [74, 75].

It is stated in the MSDS's of 2-cyanopyridine and phenol that skin contact with either of these compounds should be avoided at all costs and that they are very poisonous [74, 76].

Methanol and DMC are also dangerous compounds if ingested due to methanol poisoning [5, 77]. The dimethyl carbonate is broken down to CO<sub>2</sub> and methanol in the body so it has the same effect if ingested.

The carbon dioxide can cause unconsciousness or death at concentration of 10% or more in the air [78]. Because of the high amounts of carbon dioxide used it is possible that in case of a leak this concentration will be reached close to the ground up to a certain height. This probability increases in case of a dike around the unit or in an enclosed compartment. Carbon dioxide is heavier than air in high concentrations and thus will stay close to the ground. This concentration is not possible to see for humans and thus is very dangerous.

Water is the last chemical in the system. It is present in the lowest concentrations and also has the lowest chance for hazards [79].

## 10.2 Fire and explosion index

The fire and explosion index was calculated for the main reactor and three distillation columns. This index illustrates the dangers coming with the unit. Then some safety measurements are taken into account which lower the risks and from that the radius of exposure of each unit can be calculated (how far around the unit do other units have a risk of standing).

*Table 30:F&EI of the various units*

Unit	F&E	F&EI after safety	Radius of exposure (m)
<b>Reactor</b>	121.4	109.6	33.4
<b>Phenol extractive distillation</b>	69.6	64.1	16.4
<b>Azeotropic mixture distillation</b>	54.8	47.4	12.1
<b>Vacuum distillation column</b>	64.5	59.4	15.2

The choices made in this process are explained further in the Appendix J.1.1 along with the DOW F&EI sheets.

### 10.3 Chemical exposure index

A chemical exposure index analysis was done for a pipe rupture of the stream after the reactor. This resulted in the following perimeters:

Table 31: Chemical exposure index of methanol pipe rupture

Risk	ERPG value	Distance (m)
All individuals can stand at this distance for 1 hour without developing life threatening health effects (ERPG-3)	6551	$HD = 6551 * \sqrt{\frac{0.0798}{6551}} = 22.86$
Persons should be able to stand at this distance for 1 hour without experiencing effects that impair the person's ability to take preventive action (ERPG-2)	1310	$HD = 6551 * \sqrt{\frac{0.0798}{1310}} = 51.1$
Persons should be able to withstand this for an hour without any serious health effects (ERPG-1)	262	$HD = 6551 * \sqrt{\frac{0.0798}{262}} = 114.3$

Methanol was taken as the compound to look out for in this case, primarily because of its volatile nature and poisonous properties. The CEI is elaborated further in Appendix J.1.2.

### 10.4 Hazard and operability study (HAZOP)

A hazard and operability study (HAZOP) is carried out for one of the major unit operations. This is for the same unit as a detailed P&ID is developed in chapter 8. The HAZOP is done in order to decrease the change of a hazardous situation in the plant. HAZOP is based on the assumption that a parameter (flow, temperature, pressure, etc.) can deviate from its normal operating condition. Then the consequences of this deviation will be discussed and the incident indicators and safeguards are identified in the P&ID. If there are any present yet, then new indicators and/or safeguards need to be installed.

To discuss all deviations from all the parameters is a little too much, therefore only the most important parameters are taken to perform a HAZOP. The unit operation is the distillation column that separates methanol and DMC into pure DMC and an azeotropic mixture of methanol and DMC (T-2072).

The system has to be divided into nodes and for each node a HAZOP is carried out. In this system, the nodes are:

1. Cooling water stream for the condenser
2. Steam and condensate stream for the reboiler
3. Process streams

*The HAZOP for the different nodes are given in Table 32,*

Table 33 and Table 34.

Table 32: HAZOP for node 1: cooling water for the condenser

Project Title: PPD207_DMC					
Node 1: Condenser cooling water					
No.	Deviation	Specific Hazard Description	Potential consequences	Possible cause(s)	Incident Detectors and Safeguards
1	No flow	No cooling water	No condensation of top product, level in accumulation tank goes down	Valves closed, chiller failure	LC with low alarm, LLSD, flow indicator
2	Less flow	Less cooling water, see no flow			
3	More flow	More cooling water	More condensation of top product, more reflux	Valve misoperation	TI in top of column, flow indicator
4	Reverse flow	Is secured			
5	Two phase flow	No issue			
6	Flow other than design intent	No issue			
7	More pressure	More pressure of cooling water	Rupture of piping/gasket. Leakage, cooling water is safe, so no hazard	Thermal expansion by blocked water	Pressure relief valve
8	Less pressure	No issue			
9	More vacuum	No issue			
10	Less vacuum	No issue			
11	More temperature	Cooling water is warmer than design	See no flow	Chiller malfunction	see no flow
12	Less temperature	Cooling water is colder than design	See more flow	Chiller malfunction	See more flow
14	More level	No issue			
15	Less / No level	No issue			

Table 33: HAZOP for node 2: steam and condensate stream for reboiler

Project Title: PPD207_DMC					
Node 1: Reboiler steam					
No.	Deviation	Specific Hazard Description	Potential consequences	Possible cause(s)	Incident Detectors and Safeguard
1	No flow	No steam to reboiler	Low temperature inside the column, higher level	Valves closed	TC, TI in column, FI in stream, LC
2	Less flow	Less steam to reboiler, see no flow			
3	More flow	More steam to reboiler	High temperature in column, high pressure in column	Valves malfunction	TC, TI in column, FI in stream
4	Reverse flow	Secured by steam generator			
5	Two phase flow	No issue			
6	Flow other than design intent	No issue			
7	More pressure	Higher steam pressure	Rupture of piping, leakage. Higher temperature of steam	Valve opens	Pressure relief valve, TI in column
8	Less pressure	Lower steam pressure		Valve closes	TI in column
9	More vacuum	No issue			
10	Less vacuum	No issue			
11	More temperature	Higher steam temperature, see more pressure			
12	Less temperature	Lower steam temperature, see less pressure			
14	More level	No issue			
15	Less / No level	No issue			

Table 34: HAZOP for node 3: process streams

Project Title: PPD207_DMC					
Node 3: Process streams					
No.	Deviation	Specific Hazard Description	Potential consequences	Possible cause(s)	Incident Detectors and Safeguard
1	No flow	No feed entering the column	Pump will run on nothing, possible failure	Shut down valve closed	FI in reflux
2	Less flow	Less feed entering the column, no issue			
3	More flow	Feed exceeds capacity	Quality constraints will not be achieved	Failure of previous process units	FI in feed, possibly a storage tank in front, so not the whole column should must be shut down
4	Reverse flow	No issue			
5	Two phase flow	Two phase flow in the top and bottom product streams, reflux and after reboiler/condensatin	Liquid in top product, gas in bottom product, partially condensed top stream, partially reboiled bottom stream	LC/valve failure, to little cooling water / steam	LLSD, HLSD around LC. TI and FI in cooling water and steam lines.
6	Flow other than design intent	No issue			
7	More pressure	A higher pressure in the column	Different composition of top and bottom product, rupture of pipes, leakage	Closed valve, thermal expansion by block fluid	HPSD, PI, PC in column, FI in product streams, pressure relief valve
8	Less pressure	No issue			
9	More vacuum	No issue			
10	Less vacuum	No issue			
11	More temperature	Higher temperature in the column	Different composition of top and bottom product	Valve failure in cooling water or steam, temperature change in steam or cooling water	TI, HTSD in column, FI and TI in cooling water and steam streams
12	Less temperature	Lower temperature in the column	See 11, more temperature	See 11, more temperature	See 11, more temperature except HTSD
14	More level	Higher level in accumulator	Liquid in top product	Valve closed	LC and HLSD in accumulator
15	Less / No level	No liquid in column and accumulator	Pump failure, gas in bottom product and reboiler.	Valve failure, LC failure	LC and LLSD in column and accumulat

## 10.5 Summary

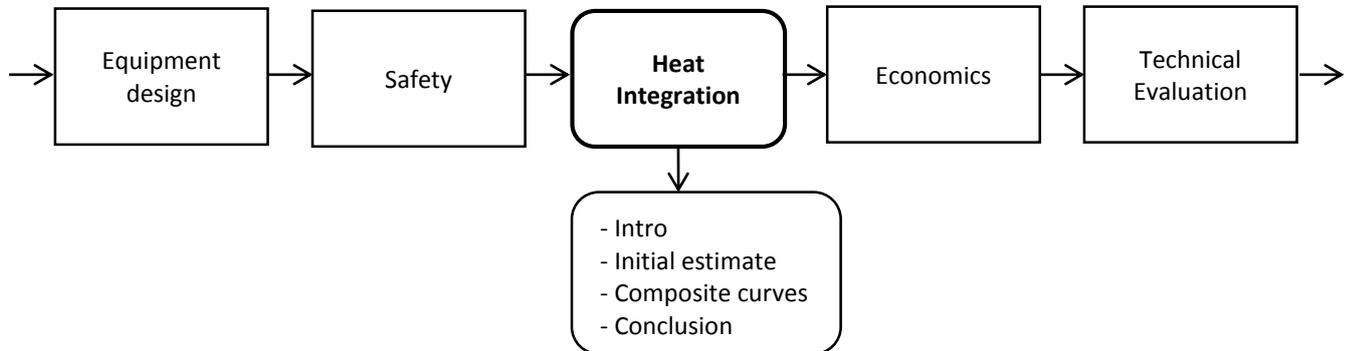
Safety considerations are always important in the process of developing a chemical process. Here, F&EI, CEI and a HAZOP are made, but only for a limited number of units. The major safety issues are discussed here.

Almost throughout the whole process, the operating temperature is above the flash point. In addition, a part of the process is operated at elevated pressure. The F&EI shows that the reactor is the most dangerous piece of equipment. Here there are compounds liquid at the operating pressure, but will be gases when the pressure is released, due to rupture for example.

Toxicity and reactivity of 2-cyanopyridine and 2-picolinamide is not fully known. For sure, 2-cyanopyridine is a toxic chemical and needs to be handled with care during the process. Also phenol is used as solvent in the extractive distillation column. Phenol is toxic and corrosive to carbon steel, therefore it is better to use a different solvent from a safety point of view.

## 11 Heat Integration

In this chapter all heating and cooling utilities are identified. Thereafter an estimation is made to identify whether these utilities show potential to be integrated to save energy costs. The used method is pinch technology.



### 11.1 Intro

First, some boundaries and assumptions need to be defined, which is done in this paragraph. The analysis is not very detailed, but gives a first insight in what possibilities are with respect to heat integration. Major assumptions are a constant specific heat capacity ( $C_p$ ) and no phase change. These assumptions are unrealistic. However, the analysis will be very complex if these assumptions are not made.

The flowsheet simulation in UNISIM is the starting point. Only coolers, heaters, condensers and reboilers are suitable for heat integration. Pumps and compressors are not, and therefore left out. The cooling utility for the reactor (R-2071) is unknown. However, the reactor is potential heating source. The overall reaction is exothermic and therefore the reactor (R-2071) needs cooling utility. Though, the operating temperature in this reactor is  $120^\circ\text{C}$ , which will not result in a high quality heating utility. The process part where the agent is recovered is not evaluated with respect to heat integration. There is not enough knowledge about this part to determine energy utilities. The required energy per utility is taken from UNISIM. To determine  $F \times C_p$ , this utility is divided by the temperature difference. For reboilers and condensers a  $\Delta T$  of 1 is used. The driving force for heat transport is a temperature difference. The minimum required temperature difference ( $\Delta T$ ) for heat exchangers is set at  $10^\circ\text{C}$ .

### 11.2 Initial estimate

A very first estimate is done based on the sum of the energy of all utilities. This is the theoretical minimum amount of energy that must be added or removed from the process. No  $\Delta T$  is taken into account. However, this is crucial because heat will not flow from a lower to a higher temperature.

The sum of energy of all suitable utilities is  $6.88\text{E}6$  kJ/h. This means that this is the bare minimum amount of energy that must be added to the process.

### 11.3 Composite curves

A list of all the equipment that is considered suitable for heat integration can be found in Appendix K. Their duties and temperature ranges are also given. The composite curve for the process is shown in Figure 19. As can be seen from the figure, there is a part which is suitable for heat integration (x-axis: ~10-23MW). An option could be to use a lower pressure in the columns, whereby the temperature in the reboiler decreases (almost straight blue lines indicate a reboiler, because  $\Delta T$  is only 1). However, some of the available 'hot' for heat integration are linked to reboilers (they cool the bottom stream of a column). Therefore, better heat integration by reducing pressure in columns is probably not possible. Feed streams for columns are heated to about the boiling point. The duty of the reboiler is hereby reduced in comparison to 'non' a preheated feed. The reason is that the temperature interval of the reboiler is less suitable for heat integration than the temperature interval of feed heater.

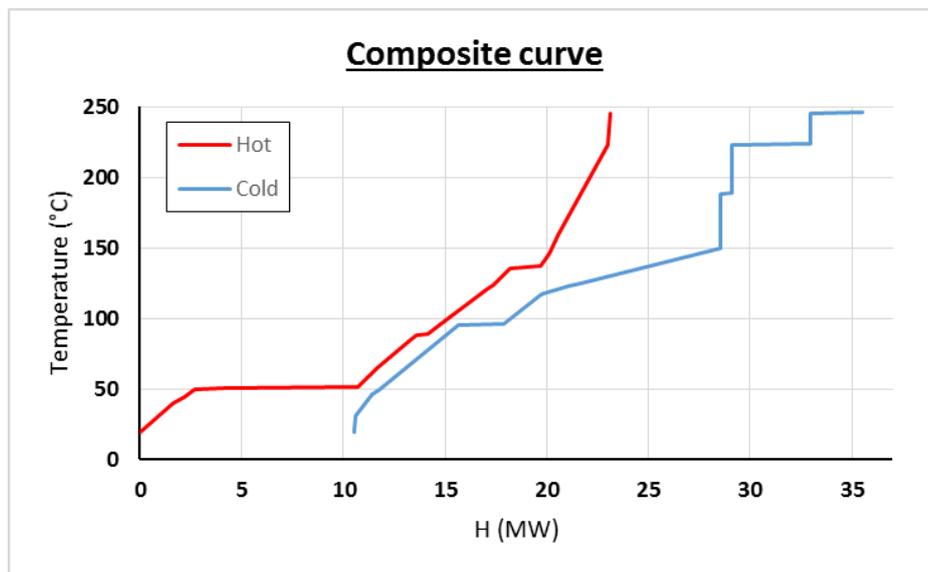


Figure 19: Composite curve, list of used heating and cooling equipment can be found in Appendix K.

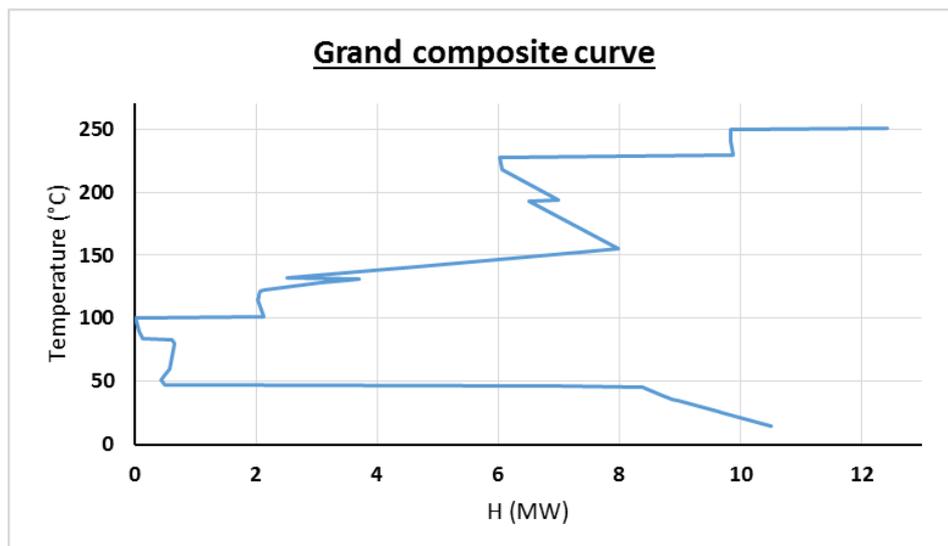


Figure 20: Grand composite curve, list of used heating and cooling equipment can be found in Appendix K.

The pinch temperature is at 100°C. The grand composite curve gives a clear view on the temperature intervals and their energy content, see Figure 20. All horizontal lines indicate either a condenser or a reboiler, because  $\Delta T$  is only 1°C. Therefore, these are easily identified. The first distillation column (T-2071) handles the biggest stream and needs by far the most amount of energy. The condenser is located at ~0.5-8.5MW, ~50°C and the reboiler at ~6-10MW, ~240°C. Above the pinch heat integration is possible up to about 3.5MW (mainly 2.5MW to 3.5MW and 6MW to 8MW). Below the pinch almost no heat integration is possible.

Cooling is in general not a big problem with respect to operating costs. When cooling water is available, only pumping costs are required.

#### 11.4 Conclusion

A proposal for a heat exchanger network was not made. Though, some conclusions, recommendations and points for discussion are drawn below.

- Above the pinch heat integration is possible up to about 3.5MW. Below the pinch almost no heat integration is possible.
- Heat with a higher temperature is more valuable than heat with a lower temperature. Therefore, preferably this 'hot' heat should be used to heat up another stream that already is quite 'hot'. For example, a stream needs an additional heater besides the heat from this 'hot' stream. Then costs can be minimized by first using the heater, and afterwards a heat exchanger to use the heat of this 'hot' stream. Shortly, the smaller the  $\Delta T$  between two streams (taking into account the minimum  $\Delta T$  required for a heat exchanger), the better. Downside is the effect on the surface area, the smaller  $\Delta T$ , the smaller the driving force, thus the heat exchanger surface area must be bigger.
- Temperature of the feed for distillation columns is optimized. Feed for the columns was heated to approximately the boiling point. Heating the feed more does not result in less overall duty. However, the temperature interval of the feed heater is lower and thus more suitable for heat integration than the temperature interval of the reboiler. In addition, lower temperature interval requires lower pressure steam, thus cheaper.
- Most of the hot streams are linked to reboilers, this are coolers of column bottom streams. Therefore, changing pressure in certain columns to optimize heat integration is probably not possible.

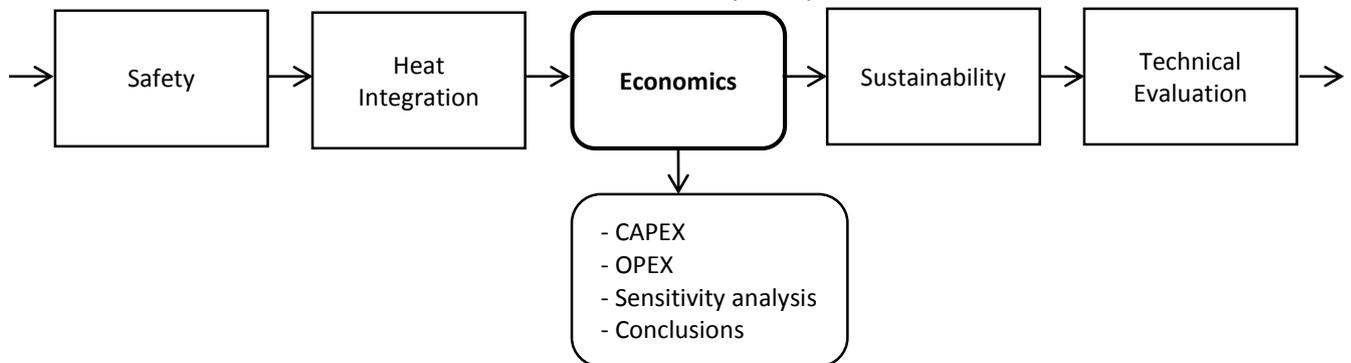
## 12 Economics

In this chapter, the economics analysis will be made for this process. First the capital expenditure (CAPEX) is determined and then the operational expenditure (OPEX) is calculated. For this the data obtained in chapter 9 of the equipment design is used. The equipment is designed in such detail that all parameters are present to make an economic evaluation. At the start of the cost estimation of each piece of equipment an overview is given of the necessary parameters. In this chapter a short overview of the CAPEX is provided, a detailed description is given in Appendix L.1.

The operational expenditure includes multiple factors of which some are elaborated in a more detail, these are raw materials (12.2.1), utilities (12.2.2), allocated capital investment (0) and wages and salaries (12.2.4). The resulting annual costs are calculated and with the sales of DMC, the annual profit is determined.

Certain aspects of the process are not fully known, the regeneration part for example, and instead of a very rough estimation, a sensitivity analysis is made. Graphs related to the sensitivity can be found in Appendix L.2.

At the end an overview and evaluation of the economic analysis is provided.



### 12.1 CAPEX

The capital expenditure is the costs of all equipment that need to be purchased in order to operate the plant. This includes units, piping, valves, storage tanks, etc. For a detailed capital investment analysis, all these aspects need to be designed in detail. This is beyond the scope of the course and to make it less complex, only the major equipment is designed in detail. Then the Lang factor method is applied. This means that first the cost of major equipment ( $C_p$ ) is calculated. Multiplying this with a certain factor, the Lang factor, compensates for all additional costs as piping, installation etc. In this evaluation the Lang factor is 6. Literature has values between 4.74 and 5.93 for fluid handling processes, but because of a recommendation from the project supervisors a value of 6 is used. [72, 80, 81]

$$CAPEX = f_L \sum_i C_{pi} \quad (12.1)$$

All major equipment need to be included in the evaluation. This means that a design is made for all heat exchangers, flash vessels, distillation columns, pumps and compressors.

An overview of the costs of the equipment without applying the Lang factor is given in Table 35.

Table 35: Total CAPEX without Lang factor

Equipment	Costs (M\$)
Heat exchangers	\$ 0.56
Flash vessels	\$ 0.47
Distillation columns	\$ 0.98
Pumps	\$ 0.14
Compressors	\$ 2.96
Reactor	\$ 0.50
<b>Total</b>	<b>\$ 5.60</b>

Filling in equation (12.1) gives:

$$CAPEX = f_L \sum_i C_{Pi} = 6 * \$5,600,000 = \$ 33,200,000$$

This cost estimation does not include the regeneration part of the process. There is not much known about this part. Therefore no design could be made for this part of the process, hence there is no possibility of making a cost estimation. In subchapter 12.3, a sensitivity analysis is made to determine the impact of the investment costs for the regeneration on the economic evaluation.

## 12.2 OPEX

The other part of the expenditure are the operational expenses (OPEX). This is all the costs needed to operate the plant. This includes raw material, utilities, depreciation of capital investment, salaries of the operators etc. In this section, the OPEX will be calculated for one year of operation. In one year the plant is estimated to operate for 8000 hours.

### 12.2.1 Raw material

In bulk chemistry, the purchase of raw material is a major part of the annual expenses. Methanol and CO<sub>2</sub> need to be purchased for the production of DMC. Also little amounts of 2-cyanopyridine and phenol are fed to the process. Table 36 gives the amount of raw material needed and the total price.

Table 36: Costs of raw material[48, 49, 51, 82]

Compound	kg/s	ton/yr	Price (\$/ton)	Total cost (M\$)
<b>Methanol</b>	11.14	3.21E+05	500	\$ 160.46
<b>CO<sub>2</sub></b>	7.63	2.20E+05	5	\$ 1.10
<b>2-Cyanopyridine</b>	0.01	4.16E+02	9150	\$ 3.81
<b>Phenol</b>	1.32E-04	3.80E+00	996	\$ 0.0038

In Figure 21 the contribution from the different raw materials on the total costs for raw materials is shown. It is clear that methanol is the determining factor for the raw materials costs. A deviation of the methanol price has a large effect on the profit.

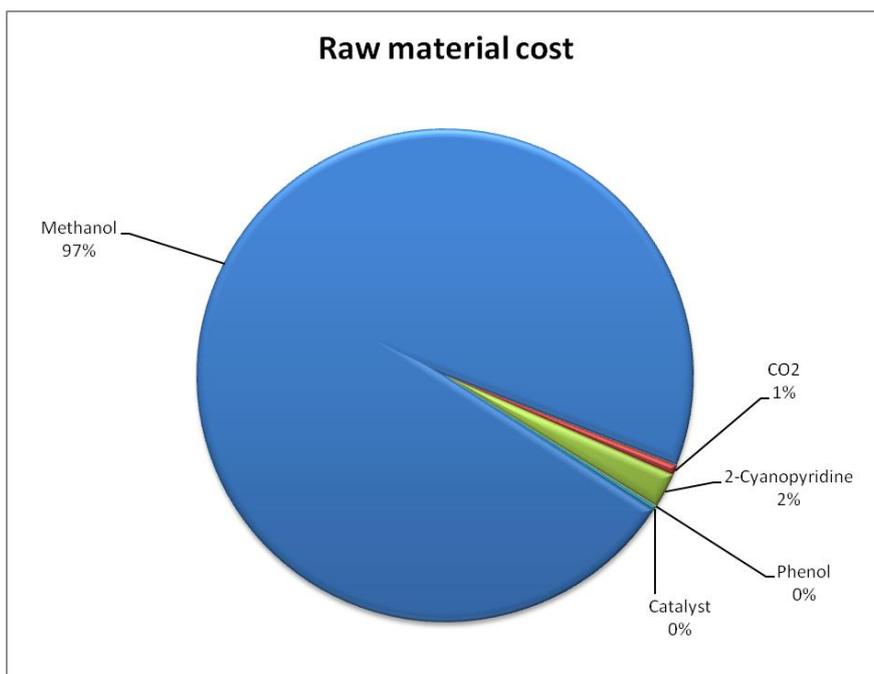


Figure 21: Cost distribution of raw materials

Ceria is used as a catalyst in the DMC reactor. It catalyses both the direct synthesis of DMC and the water removal reaction by the dehydrating agent.[7] The purchase price of ceria is between \$1,000 and \$2,000 per ton (\$1500 per ton is taken for the calculations).[83] From the reactor design, the amount of catalyst is obtained. To determine the annual price for the catalyst, the deactivation or the number of catalyst replacements per year has to be known. Bansode et al. mention little about this. Only that after 8 days, the methanol conversion drops to 40%, but nothing about the course of this deactivation.[7] This is too short and developments have to be made to increase the catalyst lifetime. For this evaluation, a replacement of catalyst of 12 times per year is assumed. In section 12.3.3 a sensitivity analysis is made to see the effect of the catalyst deactivation on the annual costs.

### 12.2.2 Utilities

Utilities do not play major role in the annual profit. The utilities are steam at different temperatures for heating, cooling water for cooling and electricity to drive pumps and compressors. During the equipment design also the required utilities are calculated. This is given in Table 37.

Table 37: Required utilities for the process. In the last column, the dimensions are rewritten in the correct units for the economic evaluation.[80]

Utilities		
<b>Chilled water</b>	5516.00 kW	1.59E+05 GJ/yr
<b>Chilled water</b>	131.22 kg/s	
<b>Cooling water</b>	430.83 kg/s	1.24E+07 m3/yr
<b>Steam low</b>	1.25 kg/s	3.61E+04 ton/yr
<b>Steam medium</b>	7.70 kg/s	2.22E+05 ton/yr
<b>Steam high</b>	2.48 kg/s	7.15E+04 ton/yr
<b>Steam very high</b>	1.53 kg/s	4.41E+04 ton/yr
<b>Electricity</b>	4729.73 kW	3.78E+04 kWh/yr

All available utilities are listed in Table 38, but the plant does not need all of them. The amounts calculated above are filled in and the annual costs of utilities is calculated, this is \$5,330,000.

Table 38: Annual costs of utilities[80]

Utilities	Price/unit	Unit	Amount	Price (M\$)
Steam very high, 595 psig	\$ 19.00	1000kg	4.41E+04	\$ 0.84
Steam high, 450 psig	\$ 14.50	1000kg	7.15E+04	\$ 1.04
Steam medium, 150 psig	\$ 10.50	1000kg	2.22E+05	\$ 2.33
Steam low, 50 psig	\$ 6.60	1000kg	3.61E+04	\$ 0.24
Electricity	\$ 0.06	kWh	3.78E+04	\$ 0.00
Cooling water (cw)	\$ 0.02	m3	1.24E+07	\$ 0.25
Process water	\$ 0.20	m3	0.00E+00	\$ -
Boiler-feed water (bfw)	\$ 0.50	m3	0.00E+00	\$ -
Refrigerator, -150 F	\$12.60	GJ	0.00E+00	\$ -
Refrigerator, -90 F	\$ 10.30	GJ	0.00E+00	\$ -
Refrigerator, -30 F	\$ 7.90	GJ	0.00E+00	\$ -
Refrigerator, 10 F	\$ 5.50	GJ	0.00E+00	\$ -
Chilled water, 40 F	\$ 4.00	GJ	1.59E+05	\$ 0.64
Natural gas	\$ 0.14	SCM	0.00E+00	\$ -
Fuel oil	\$ 400.00	m3	0.00E+00	\$ -
Coal	\$ 66.00	1000kg	0.00E+00	\$ -
Wastewater treatment	\$ 0.33	kg organic removed	0.00E+00	\$ -
Landfill	\$ 0.17	drykg	0.00E+00	\$ -
<b>Total</b>				<b>\$ 5.33</b>

Stearns contributes the most to the utility price. Heat integration is not yet applied in the process, therefore the amounts of steam can be decreased and the utility price can significantly decrease. The contributions of the different utilities to the annual utility costs is schematically shown in Figure 22.

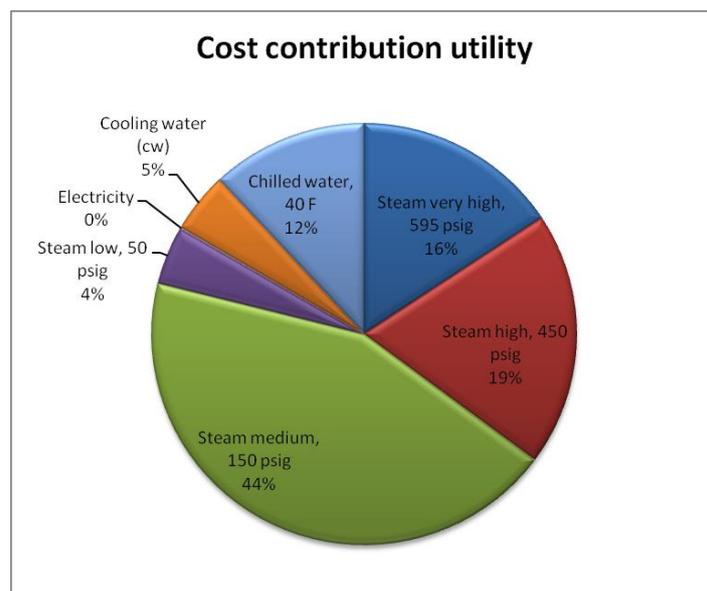


Figure 22: Contributions of the different utilities to the total utility price

### 12.2.3 Allocated investment costs

Utilities are produced somewhere at the same site. Therefore some investments in the utility plants associated with this production are needed. A quick estimation can be made for this investment costs. Depreciation of this investment will then be added to the annual costs. For the calculation of this additional investments a size factor is needed for every utility. Slow and Shigh are the boundaries for the size factor given in the second column of Table 39. The sixth column gives the calculations for the allocated investment costs. The estimated allocated investment costs are a little over 19 million dollars.[80]

Table 39: Allocated capital investment costs for utility plants

Utility	Unit	Slow	Shigh	S	Equation	Allocated costs (M\$/yr)
Steam	lb/hr	2.00E+03	1.00E+06	1.03E+05	$820 * S^{0.81}$	\$ 9.42
Electricity	MW	5.00E-01	1.00E+03	4.73E+00	$2,600,000 * S^{0.83}$	\$ 9.44
Cooling water	gpm	1.00E+03	2.00E+05	6.83E+03	$1,000 * S^{0.68}$	\$ 0.40
Process water	gpm	5.00E+00	1.00E+04	0.00	$1,500 * S^{0.96}$	\$ -
Refrigeration	Tons	3.00E+00	1.00E+03	0.00	$11,000 * S^{0.77}$	\$ -
<b>Total</b>						<b>\$ 19.26</b>

### 12.2.4 Wages and salaries

A part or the annual production costs are the wages, salaries and benefits for the operators, technical assistance and control laboratory. Operators work in 5 shifts and 2,080 hours per year. In a continuous operation of a fluid processing plant with a 450kton/yr production, the number of operators is 2 per plant section. In the process there are two reactor sections and two separation trains. This means 4 sections and 8 operators per shift. The total cost for wages and salaries will be \$4,500,000 per year, as shown in Table 40.[80]

Table 40: Wages and salaries

Operations	Price per unit	Unit	Amount	Costs (M\$/yr)
Direct wages and benefits (DW&B)	\$ 35.00	operator-hr	83200	\$ 2.91
Direct salaries and benefits	15% of DW&B		-	\$ 0.44
Operating supplies and services	6% of DW&B		-	\$ 0.17
Technical assistance to manufacturing	\$ 60,000.00	operator/shift	8	\$ 0.48
Control laboratory	\$ 65,000.00	operator/shift	8	\$ 0.52
<b>Total</b>				<b>\$ 4.50</b>

### 12.2.5 Annual cost and profit

An overview of the annual costs for the production plant is given in Table 41. The total production costs is approximately \$220,000,000. Raw material has by far the highest expenses, about 90% of the total cost of manufacture.[80] Schematically this is shown in Figure 23.

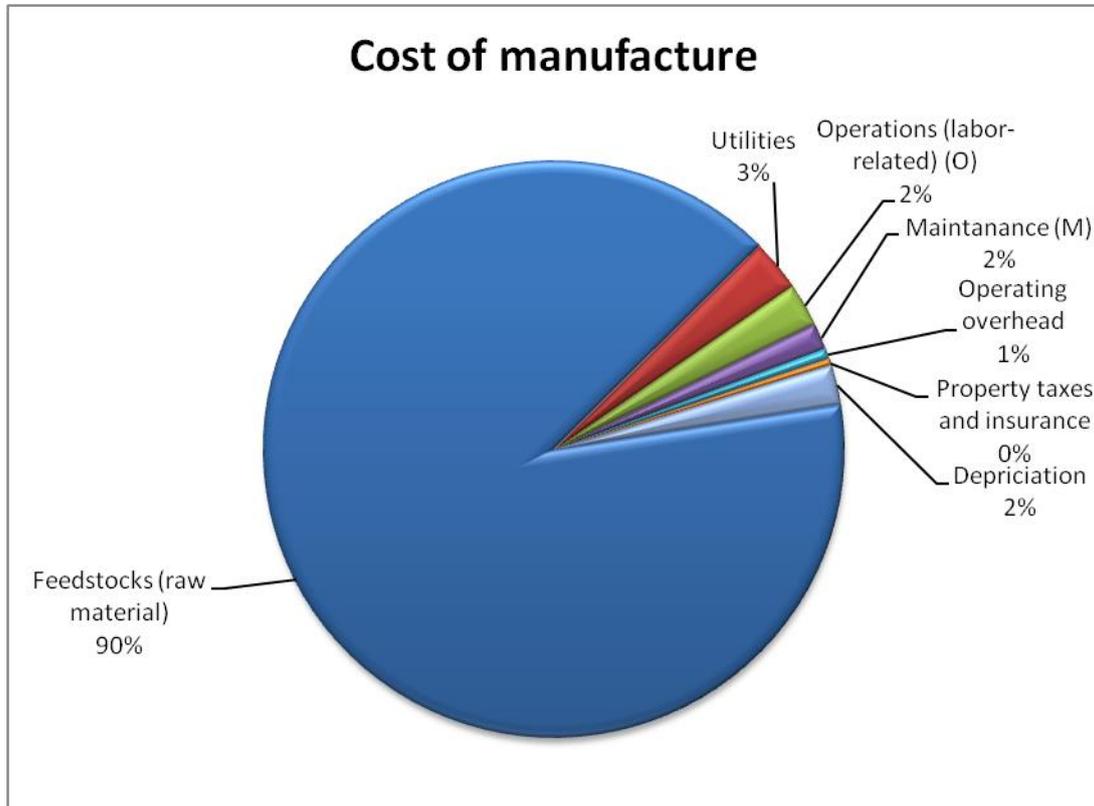


Figure 23: Contributions of the cost factors on the cost of manufacture

DMC is the only product to be sold. The price of DMC is \$700 per ton and the annual production is set at 450kton. This means the income from sales will be \$315,000,000.[84]

Then the profit before taxes will be:

$$\text{Profit} = \$315,000,000 - \$220,000,000 = \$95,000,000 \quad (12.2)$$

Table 41: Overview of the annual costs (in million dollars)[80]

Cost factor	Typical cost	unit	Amount		Total (M\$/yr)
Feedstocks (raw material)					\$ 165.86
Utilities					\$ 5.33
<i>Steam very high, 595 psig</i>	\$ 19.00	1000kg	4.41E+04	\$ 0.84	
<i>Steam high, 450 psig</i>	\$ 14.50	1000kg	7.15E+04	\$ 1.04	
<i>Steam medium, 150 psig</i>	\$ 10.50	1000kg	2.22E+05	\$ 2.33	
<i>Steam low, 50 psig</i>	\$ 6.60	1000kg	3.61E+04	\$ 0.24	
<i>Electricity</i>	\$ 0.06	kWh	3.78E+04	\$ 0.00	
<i>Cooling water (cw)</i>	\$ 0.02	m3	1.24E+07	\$ 0.25	
<i>Process water</i>	\$ 0.20	m3	0.00E+00	\$ -	
<i>Boiler-feed water (bfw)</i>	\$ 0.50	m3	0.00E+00	\$ -	
<i>Refrigerator, -150 F</i>	\$ 12.60	GJ	0.00E+00	\$ -	
<i>Refrigerator, -90 F</i>	\$ 10.30	GJ	0.00E+00	\$ -	
<i>Refrigerator, -30 F</i>	\$ 7.90	GJ	0.00E+00	\$ -	
<i>Refrigerator, 10 F</i>	\$ 5.50	GJ	0.00E+00	\$ -	
<i>Chilled water, 40 F</i>	\$ 4.00	GJ	1.59E+05	\$ 0.64	
<i>Natural gas</i>	\$ 0.14	SCM	0.00E+00	\$ -	
<i>Fuel oil</i>	\$ 400.00	m3	0.00E+00	\$ -	
<i>Coal</i>	\$ 66.00	1000kg	0.00E+00	\$ -	
<i>Wastewater treatment</i>	\$ 0.33	kg organic removed	0.00E+00	\$ -	
<i>Landfill</i>	\$ 0.17	drykg	0.00E+00	\$ -	
Operations (labor-related) (O)					\$ 4.52
<i>Direct wages and benefits (DW&amp;B)</i>	\$ 35.00	operator-hr	83200	\$ 2.91	
<i>Direct salaries and benefits</i>	15% of DW&B		-	\$ 0.44	
<i>Operating supplies and services</i>	6% of DW&B		-	\$ 0.17	
<i>Technical assistance to manufacturing</i>	\$ 60,000.00	operator/shift	8	\$ 0.48	
<i>Control laboratory</i>	\$ 65,000.00	operator/shift	8	\$ 0.52	
Maintenance (M)					\$ 2.70
<i>Wages and benefits (MW&amp;B)</i>	3.5% of CTDC		-	\$ 1.18	
<i>Salaries and benefits</i>	25% of MW&B		-	\$ 0.29	
<i>Materials and services</i>	100% of MW&B		-	\$ 1.18	
<i>Maintenance overhead</i>	5% of MW&B		-	\$ 0.06	
Operating overhead					\$ 1.10
<i>General plant overhead</i>	7.1% of M&O-SW&B		-	\$ 0.34	
<i>Mechanical department services</i>	2.4% of M&O-SW&B		-	\$ 0.12	
<i>Employee relations department</i>	5.9% of M&O-SW&B		-	\$ 0.28	
<i>Business services</i>	7.4% of M&O-SW&B		-	\$ 0.36	
Property taxes and insurance	2% of CTDC		-		\$ 0.67
Depreciation					\$ 4.05
<i>Direct plant</i>	8% of (CTDC - 1.18Calloc)		-	\$ 2.69	
<i>Allocated plant</i>	6% of 1.18Calloc		-	\$ 1.36	
<i>Rental fees (Office and lab space)</i>	(No guideline)		-	\$ -	
<i>Licensing fees</i>	(No guideline)		-	\$ -	
<b>COST OF MANUFACTURE (COM)</b>					<b>\$ 184.24</b>
General expenses					\$ 36.38
<i>Selling (of transfer) expenses</i>	3% (1%) of sales		-	\$ 9.45	
<i>Direct research</i>	4.8% of sales		-	\$ 15.12	
<i>Allocated research</i>	0.5% of sales		-	\$ 1.58	
<i>Administrative expense</i>	2% of sales		-	\$ 6.30	
<i>Management incentive compensation</i>	1.25% of sales		-	\$ 3.94	
<b>TOTAL GENERAL EXPENSES (GE)</b>					<b>\$ 36.38</b>
<b>TOTAL PRODUCTION COST</b>	COM + GE				<b>\$ 220.62</b>

### 12.2.6 Evaluation

A profit can be obtained of 95 million dollars per year, however this needs some nuance. In the process the formation of side products is neglected. This means that the overall conversion is almost 100%. As cheap CO<sub>2</sub> is converted into expensive DMC, there is a large margin. There are three important factors not completely included in the calculation.

The first is the loss of dehydrating agent. A selectivity of 100% is assumed, in reality it is very high, but 100% will not be reached. 2-cyanopyridine is a very expensive compound and the exact effect of the dehydrating agent loss is further investigated in the next section.

All costs related to the regeneration part are not taken into account, there is just too little information about it. This has effect on the utility, capital investment and selectivity of the regeneration reaction. So, this effects the profit and return rate of the investment.

The profit of 95 million is without taxes. The tax rate depends on the country where the facility is located. Regardless, this will be a big part of the profit.

#### 12.2.6.1 Profitability

The profitability is an important measure for the management to approve an investment. In order to make an analysis the tax rate has to be known. Assuming the plant is located in the United States, the tax rate is estimated at 40% of the profit[80]. Then the profit after taxes will be approximately \$57,000,000. Two profitability measures will be used in here; the return on investment (ROI) and the payback period (PBP).

The ROI can be determined with equation (12.3), where the profit after taxes need to be used.[80]

$$ROI = \frac{Profit}{C_{TCI}} \quad (12.3)$$

$C_{TCI}$  is the total capital investment. This is not only the CAPEX, but also includes starting capital and working capital. Working capital includes cash reserve for 30 days (8.33% of cost of manufacture), one week of inventories of liquid and solid products (1.92% of sales) and the difference between 30 days of accounts receivable (8.33% of sales) and 30 days of accounts payable (8.33% of raw material).[80]

$$C_{WC} = \text{cash reserves} + \text{inventory} + \text{accounts receivable} - \text{accounts payable} \quad (12.4)$$

Starting capital is estimated as 2% of the CAPEX. Then equation (12.5) becomes:[80]

$$ROI = \frac{Profit}{CAPEX + C_{WC} + C_{SC}} = 84\% \quad (12.5)$$

This means 84% of the investment is returned in one year of operation.

The second measure for the profitability is the payback period. This is number of years to earn the CAPEX, from equation (12.6) it is a little over half a year.[80]

$$PBP = \frac{CAPEX}{Profit + Depreciation} = 0.55 \text{ yr} \quad (12.6)$$

### 12.3 Sensitivity analysis

Sensitivity analyses are generally applied to investigate the effect of a parameter that is not very accurate or in this case not known at all. If the profitability is highly affected by this parameter, further research is needed. A small effect on probability means that the conclusions of the original results will not change when further research determines the exact costs.

In this section four sensitivity analyses are carried out; recovery of dehydrating agent, investment costs for the regeneration, catalyst deactivation and the methanol price. Methanol accounts for 73% of the total costs, therefore the profitability will strongly depend on the methanol price. It would be interesting to see how the possible deviations from the original \$500 per ton effect the profit.

The sensitivity can be calculated with equation (12.7). Here the effect of a dependent variable (x) on the independent variable (y) can be determined. In this case the independent variable is the profit before taxes. This will only work if the original value is not equal to 0. So, for the capital investment of the regeneration and the dehydrating agent loss this cannot be done.

$$S = \frac{\frac{\delta y}{\delta x}}{\frac{y}{x}} = \frac{\frac{y_1 - y_0}{x_1 - x_0}}{\frac{y_0}{x_0}} \quad (12.7)$$

#### 12.3.1 Dehydrating agent recovery

The price of 2-cyanopyridine is very high, \$9150/ton. In the simulations of the process, the selectivity of 2-cyanopyridine is taken as 100%. Only in the separations steps, some dehydrating agent is lost and ended up in the DMC product. For the regeneration also the selectivity should be very high, to determine the overall impact of the loss of dehydrating agent on the profitability, a sensitivity analysis is made. The effect of the loss of agent on the profit before taxes is shown in Figure 24 and the payback period is shown in Figure 25.

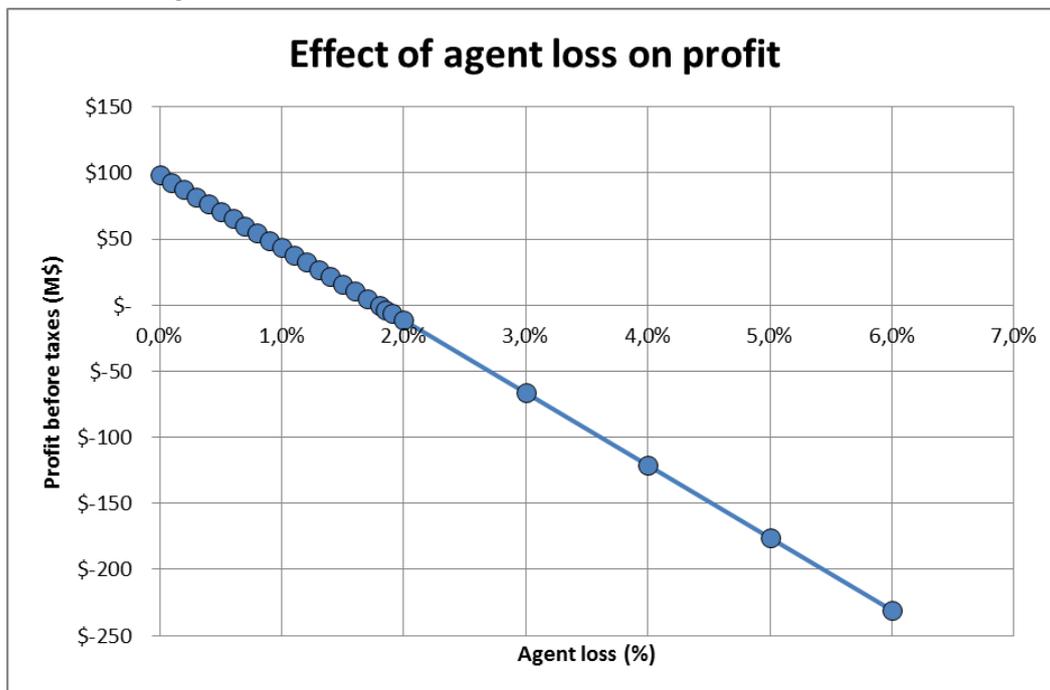


Figure 24: Effect of dehydrating agent loss on the profit

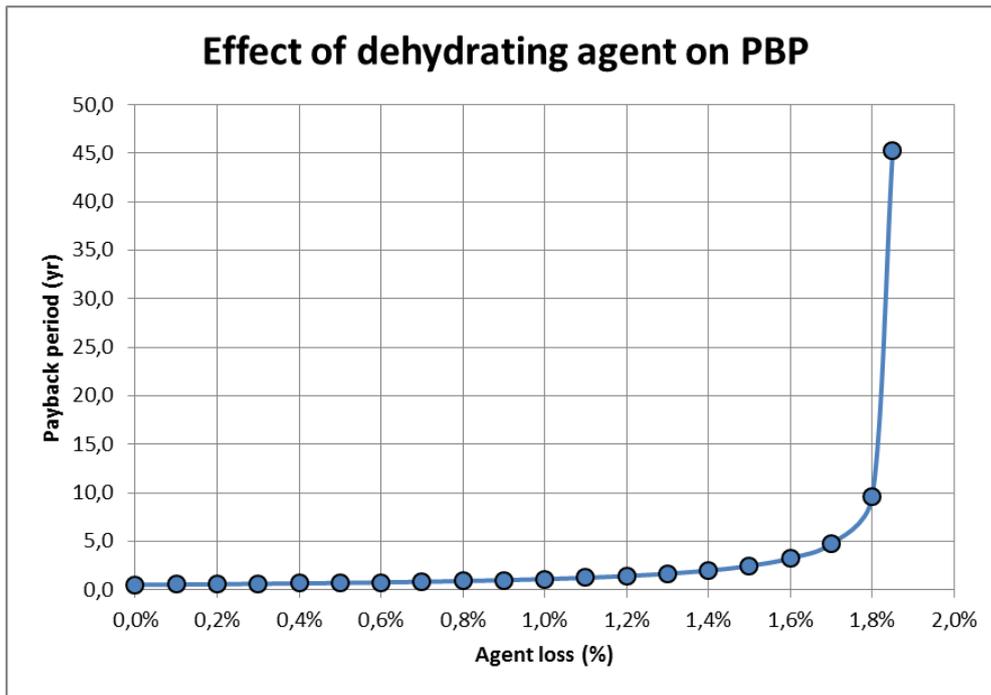


Figure 25: Effect of dehydrating agent on payback period

### 12.3.2 Regeneration investment costs

In the CAPEX calculations, the regeneration part is not taken into account. Due to the lack of data it there is no possibility of estimating the capital investment of this part. Therefore, the effect of the capital investment for this part is investigated.

The relative costs for regeneration are the costs compared to the CAPEX of the rest of the process. Figure 26 shows its influence on the profit before taxes and Figure 27 gives the return of investment.

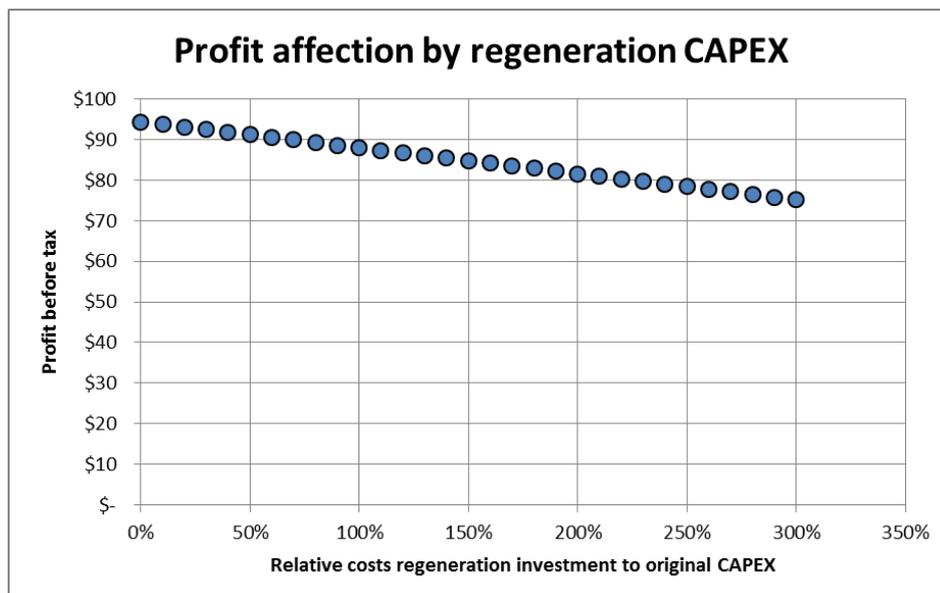


Figure 26: Influence of capital investment of the regeneration section on the profit before taxes. At 0% the original situation applies.

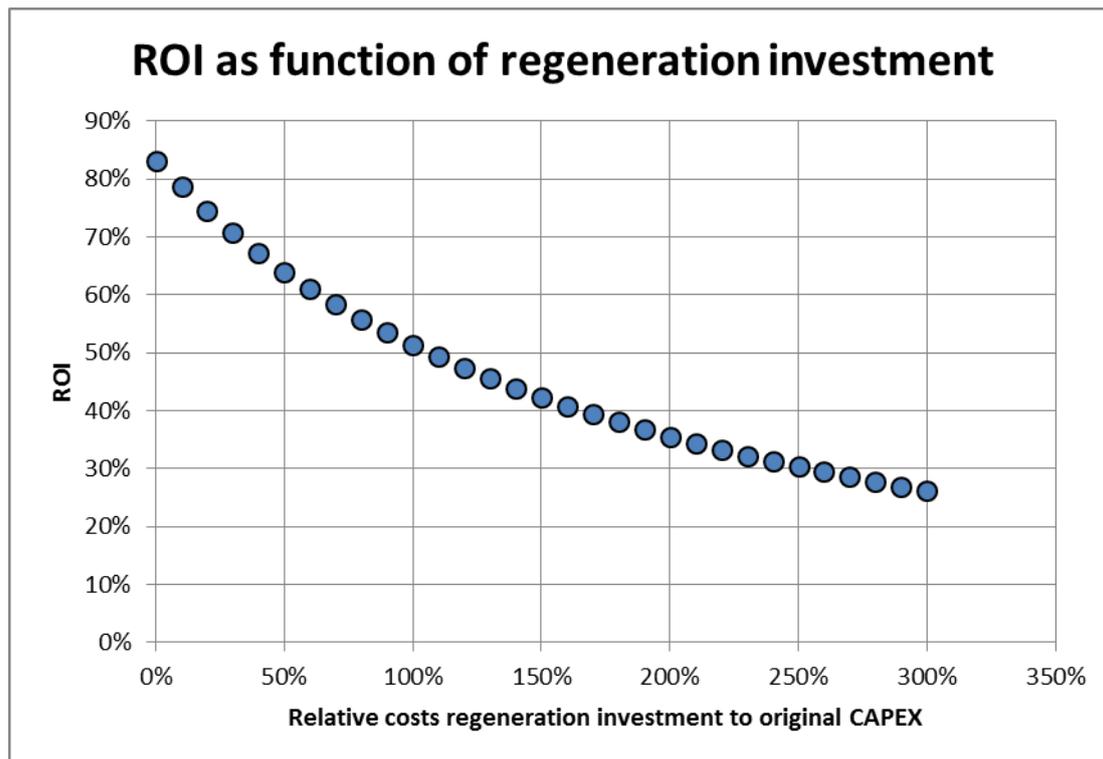


Figure 27: Return of investment as function of the capital investment for regeneration

### 12.3.3 Catalyst deactivation

Catalyst deactivation is an issue that needs further research. However, the impact of the catalyst deactivation can be investigated. In the economic evaluation, it is assumed that the catalyst needs to be replaced once a month. Extra reactor shells are placed to easily switch between operating mode and catalyst replacement mode. With expensive catalyst, the profitability could be very sensitive to the frequency of catalyst replacement. Fortunately, the ceria catalyst is not very expensive. The sensitivity of the replacement frequency on the profit is calculated:

$$S = \frac{\frac{\delta y}{\delta x}}{\frac{y}{x}} = -0.0052 \quad (12.8)$$

In Appendix L.2.3. detailed curves with the replacement of catalyst influence on profit, ROI and PBP can be found. The sensitivity analysis shows that a the replacement of catalyst does not affect the profit much. In this sensitivity analysis only the catalyst costs for the replacement of catalyst are taken into account, not the labour that is required to replace it.

#### 12.3.4 Methanol price

Methanol costs account for almost 75% of the total annual costs. A fluctuation in the methanol price, could have serious consequences for the profitability of the process. The sensitivity is analysed in this section. Graphs with the effect on ROI, PBP and profit can be found in Appendix L.2.4. The sensitivity is calculated for the methanol price on the annual profit.

$$S = \frac{\frac{\delta y}{y}}{\frac{\delta x}{x}} = -1.70 \quad (12.9)$$

A sensitivity of -1.70 means a large impact on the profit as the methanol price varies. Figure 28 shows the methanol price development. There were some big deviations in the past decades, but the expectation is a slight increase in the next years.[85]

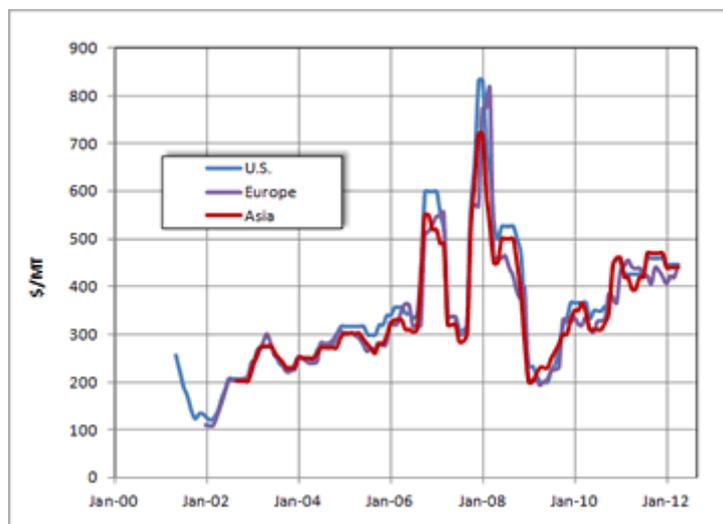


Figure 28: World methanol price development[85]

#### 12.4 Conclusions

The conclusions are based on the calculations made in this chapter. First the CAPEX is determined with the Lang factor method. Details can be found in Appendix L.1. Then the OPEX is calculated, where some aspects are explained in more detail. With this the profit and profitability is determined. Uncertainties are further examined in terms of a sensitivity analysis. Now the results of these evaluations are discussed.

##### 12.4.1 CAPEX

The CAPEX for this process is about 33 million dollars. For a large scale production facility this is very cheap. Main reason is that the equipment is small. Large streams are separated into small streams early in the process and therefore significantly reducing equipment sizes. Compressors contribute the most (~53%) to the capital investment.

In addition, the investment for the regeneration section should be included. Due to a lack of data, this is not done yet. There is no detailed process design developed, only a conceptual design. Therefore the CAPEX will go up, but an estimation cannot be made.

#### 12.4.2 OPEX

The OPEX is estimated at \$220 *mln* per year. Purchase costs for methanol account for 73% of the OPEX and all raw materials together are 75% of the total annual costs. Here the catalyst costs are included for a once per month replacement of catalyst.

The prices for raw materials are current prices, 2-cyanopyridine needs to be purchased in relatively large amounts, as it is not a bulk chemical. If such a process develops to an industrial large scale process, the market will react. Supply and demand curves change and prices of raw material might go up and the DMC price might go down. Especially for a specialty chemical as 2-cyanopyridine, this could be the case.

Utilities are only 2% of the total expenses of the plant. As with the CAPEX this has to do with the relatively small equipment. Lowering the utilities is definitely possible. Heat integration is not applied yet and all coolers, heater, condensers and reboilers are operated with steam or cooling water. Also some coolers need to cool down even further and chilled water is needed. Chilled water is much more expensive than cooling water and a significant reduction in utility can be obtained, if it would be possible to use cooling water for all coolers.

#### 12.4.3 Profit

The sales of DMC are \$315 million per year, with the annual costs this results in a profit before taxes of \$95 million. In combination with the return of investment (84%) and payback period (0.55 yr), every company in the world would build this plant. Raw materials contribute the most to the costs. Methanol is not very expensive and CO<sub>2</sub> is almost free, this is converted into more expensive DMC. Agent loss in the regeneration section and formation of side-products are not included and all investments for the regeneration are not taken into account. So, even in the most perfect situation a profit of \$95 million is not realistic. How these unknowns affect the profit is evaluated in the sensitivity analysis in the next section.

#### 12.4.4 Sensitivity

In section 12.3, the sensitivity of certain parameters on the profitability is investigated. These are the loss of 2-cyanopyridine during the process, capital investment for the regeneration of dehydrating agent, frequency of catalyst replacement and the methanol price.

Loss of dehydrating agent has a major effect on the profitability. Due to the high price of 2-cyanopyridine, the loss can only be about 1.7% to make a profit. However, the payback period and return of investment are too low at that point. A maximum of 1.4% is reasonable, to obtain a good PBP (2 yr) and ROI (19%). From this maximum loss it can be concluded that the dehydrating agent plays an important role in the profitability of the process. The selectivity in the first reactor is not absolutely 100% and also in the separation section some dehydrating agent is lost. This leaves a narrow margin for agent loss in the regeneration part. If it is not possible to obtain an allowable recovery, an option is to develop a production process for 2-cyanopyridine at larger scale. In this way the 2-cyanopyridine price could be decreased and profitability of the DMC production will be increased.

The investment for the regeneration part does not have a big influence on the annual costs. Even for an investment of three times the current CAPEX, the profit is still above the \$70 million dollars per year. A bigger influence is expected in the ROI and PBP. Comparing to the base case (0%), a significant decline in ROI and PBP is obtained, but still within reasonable ranges.

The catalyst deactivates rather quickly and a catalyst replacement of 12 times per year is taken as first estimate. A sensitivity analysis is carried out with respect to this 12 replacements per year. Figures in Appendix L.2.3 show little influence on the profitability. A sensibility of -0.0052 confirms the little effect of catalyst replacement.

Purchase as methanol is the main costs of the process, about 73%. A strongly deviating price, may influence the profitability. Therefore the sensitivity is determined, with \$500/ton as base price. the sensitivity is calculated as -1.70. This means for a 10% increase in methanol price, the profit will drop with 17%. An unstable methanol market will definitely cause some caution to invest in such a process. The maximum price to realize a profit is \$775/ton, that is 45% increase in price. For the next years the price of methanol will probably rise a little, but not at a concerning rate.

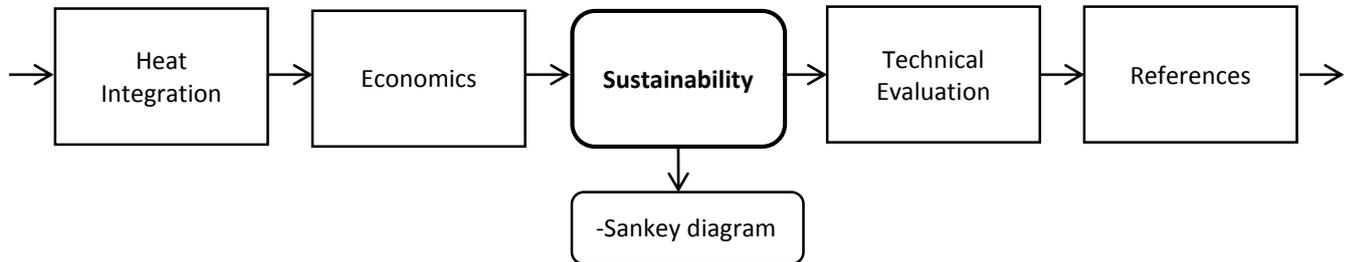
#### 12.4.5 Summary

The most important conclusion drawn regarding the economics of this DMC production process are:

- Small equipment results in low capital investment, about \$33,000,000
- Annual costs are estimated at \$220,000,000 with a 75% contribution from raw material purchase
- The maximum annual profit is \$95,000,000, with the remark that the regeneration is not included in the cost calculation
- The high price of dehydrating agent makes it absolutely necessary to limit the loss of it during the process. A maximum loss of 1.4% is determined
- Profitability strongly depends on the price of methanol, the sensitivity is -1.70
- Investment costs of the regeneration and catalyst replacement are not important factors for the profit, ROI and PBP.

## 13 Sustainability

In this chapter a Sankey diagram with mass and energy flows is given. Thereby the process streams are evaluated. A Sankey diagram of the carbon balance was not made, because all the feed ends up in products or is recycled. In addition, by-products were not taken into account and no purges were used.



### 13.1 Sankey Process diagram

A Sankey diagram was made of the process to visualize the size of the mass and energy streams, see Figure 29. The blocks in the figure indicate important unit operations or a cluster of unit operations. Energy streams with respect to the reactor are unknown. Nonetheless, the reaction should release heat, and therefore the reactor should be cooled. Each compound and energy type is indicated by a colour; see the legend in Figure 29. Energy input for the reactor and regeneration section are unknown and therefore not displayed (R-2071, R-2072, T-2075, T-2076).

There are several interesting aspects in this figure. The biggest flows are separated first. Thus, the unit operations that are further in the process only have to process a smaller stream, which is beneficial with respect to OPEX and CAPEX. In addition, 97% of the CO<sub>2</sub> is recycled immediately after the reaction. Thereby the volume flow is drastically reduced due to the fact that CO<sub>2</sub> is gaseous. Already in two separation steps the mass flow is reduced from 2.40E5 to 6.23E4 kg/h (factor 3.9). Already in the third step DMC with the final spec is obtained, whereby the total mass flow again drastically is reduced.

From the energy flows towards the separation steps (drawn as an arrow pointing at the blocks) can be seen whether separation steps are energy intensive or not. The first step (F-2071), is relatively easy. It was constructed in a way so that pressure drop is minimal. As a result, compression and thus energy costs are minimized. T-2071 and T-2072 are energy intensive, both are distillation columns that process a very big stream. T-2073 requires a lot of energy when taken into account the relatively small stream it treats. This is the extractive distillation column and therefore a relatively difficult separation. Though, the solvent recovery (T-2074) is relatively easy.

Overall the process seems quite efficient with respect to the mass and energy streams.

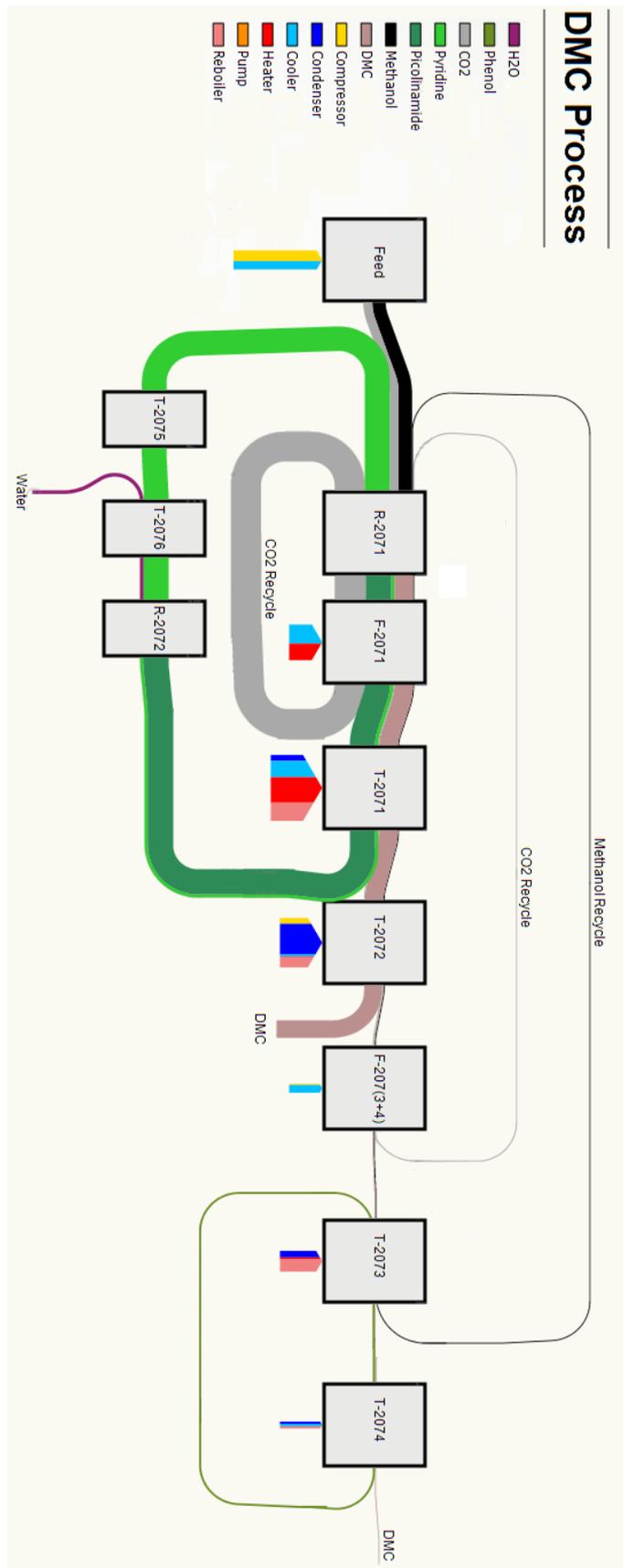
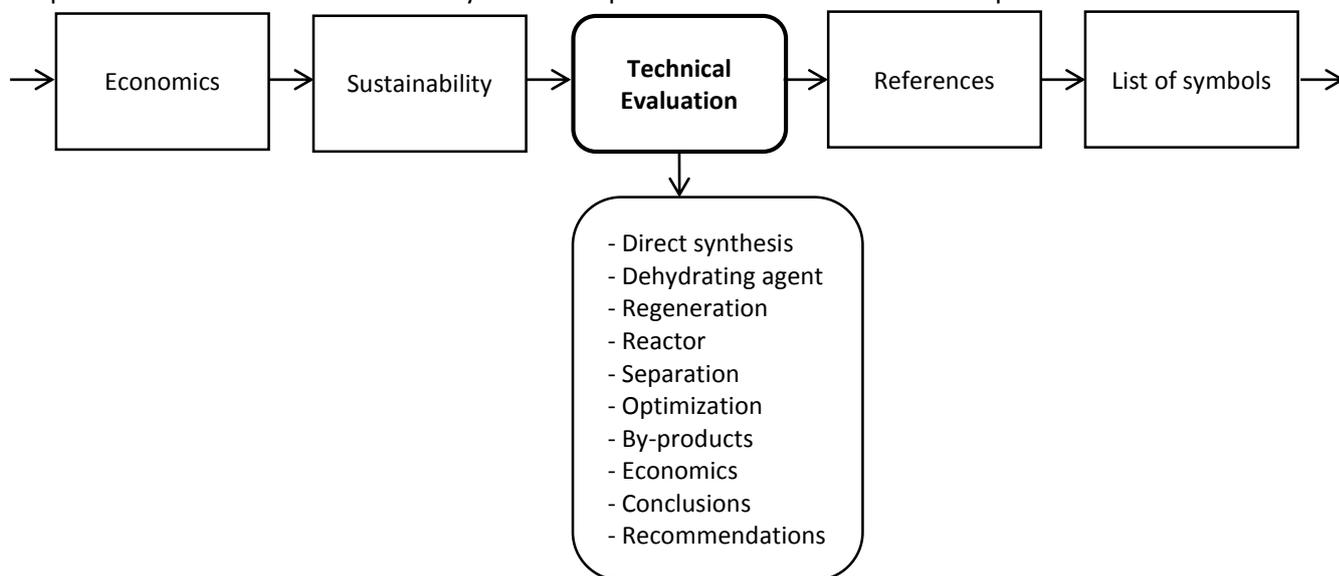


Figure 29: Sankey diagram of the overall process. Mass flows are displayed. In addition, energy streams to separation units are displayed as arrows.

## 14 Technical evaluation

The direct synthesis of DMC from methanol and CO<sub>2</sub> gains increasing interest, as was mentioned in the scope. Main limitations for the viability for such a process are discussed in this chapter.



### 14.1 Direct synthesis

The single pass conversion (~1%) for the production of DMC from methanol and CO<sub>2</sub> is too low to develop a viable process. Therefore, strategies to enhance the conversion were investigated. It was chosen to remove the water from the reaction mixture whereby the equilibrium shifts and thus the conversion is enhanced. Therefore, it was decided to use a dehydrating agent to remove the water. This can be carried out at the desired reaction conditions and is able to significantly shift the equilibrium towards the product side. A wide variety of possible agents were investigated and 2-cyanopyridine was finally chosen.

### 14.2 Dehydrating agent

According to Bansode et al. and Honda et al. the usage of 2-cyanopyridine as a dehydrating agent results in a very high single pass conversion of methanol (92.4% at 120°C and 30bar), with a selectivity of 99% [7]. Also this reaction can be catalysed with the same catalyst as the synthesis of DMC, namely cerium oxide. As a result the reactor configuration will be a lot less complex.

However, hardly anything is known about the reverse reaction, converting 2-picolinamide back to 2-cyanopyridine. Only Honda et al. show that it is possible to do this reverse reaction [6]. Though, it is on lab scale and the timescale needed is in the order of days [6]. In any case, a breakthrough is needed here. Especially considering the costs of the dehydrating agent. In the economical evaluation of the process, it shows that only a loss of 1.4% is acceptable. The regeneration of dehydrating agent is therefore a crucial part of the process.

Furthermore, the agent compounds are not very common chemicals, as a result more specific properties are unknown. The unknown properties are estimated and this may lower the accuracy of the UNISIM model in terms of solubility and gas-liquid equilibrium. Especially the solubility of 2-picolinamide in DMC and methanol is interesting. A good solubility may reduce or eliminate transportation problems of high melting compounds as 2-picolinamide (110°C)

An extensive literature search for another dehydrating agent did not result in a better alternative. The most important criteria for the options to meet are:

- Able to react with water under the operating conditions
- Very selective to water, as there is very little water present
- High conversion and overall selectivity towards DMC
- Reverse reaction is possible within a realistic timeframe and conditions
- Fast reaction with water

Unfortunately, none of the options could meet all these criteria and the choice is made to resume with 2-cyanopyridine.

### 14.3 Regeneration

As stated in previous paragraphs, regeneration is not considered in this project. The main reason is the lack of literature describing this reaction. It was not possible to construct a plausible process, with only this data.

### 14.4 Reactor

A mathematical reactor model was set up to give some insights in the size that is required to scale up the reactor used in the article of Bansode et al. Three phases are present and therefore a co-current trickle-bed reactor is used. Conclusions are based on the model; however the model is based on quite some assumptions and not completely validated with experimental data.

Hatta analysis and the reactor model showed that the system is reaction limited. When this is the case, the excess of CO<sub>2</sub> can probably be lowered. Literature does not report significant temperature rises, probably due to the small reactor size (1.74mm diameter, 7.5cm)[7]. However, according to thermodynamics the heat effects are quite significant, T<sub>ad</sub>=232°C and should be considered when scaling up.

Bansode et al. report a high weight time yield of ca. 1 g<sub>DMC</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, with a conversion of 92.4% and a selectivity of >99% [7]. Altogether, these are promising results.

Testing the influence of impurities in the feed with this model would be interesting. In this report the assumption was made that recycling DMC to the reactor is very unfavourable for its performance. Though, this is questionable when a dehydrating agent is used. In case recycling a certain amount of DMC back to the reactor is acceptable, then this may alter the separation section.

Bansode et al. report a conversion of only 40% after 200h, though selectivity remains the same [7]. Why and how this happens is unknown. However, it can be concluded that catalyst deactivation happens rapidly. Although the frequency of catalyst replacement do not show a significant effect on the profitability, further research to enlarge catalyst lifetime is required.

## 14.5 Separation

In this paragraph, only the difficulties for separation within the current process and its boundaries are discussed.

### 14.5.1 Azeotrope

Separating DMC from methanol is challenging, due to the azeotrope point present at 0.85 mole fraction methanol. The decision to first distil the mixture to the azeotropic point, obtain DMC pure at the bottom and then use extractive distillation to recover the last DMC paid off. The large DMC stream (#17) is separated and a relatively small stream (#16, about 8x smaller) undergoes extractive distillation. Relatively small equipment is able to obtain pure DMC as product and pure methanol for the recycle.

### 14.5.2 CO<sub>2</sub> issues

In the first two flash vessels, the major part of the CO<sub>2</sub> is recycled immediately (97%). However, quite some of it is still dissolved in DMC and methanol. This gives issues in the condensation of the top product at distillation columns. Then there is CO<sub>2</sub> present in higher amounts and liquefaction is not possible, therefore all columns with CO<sub>2</sub> have a gaseous top product.

In the stream before extractive distillation CO<sub>2</sub> gets concentrated (37%) and eventually will end up in the methanol recycle. (As it cannot be liquefied under normal circumstances, a compressor would be needed for this recycle). Besides, methanol is a liquid and CO<sub>2</sub> is gas at reactor conditions, so this also gives problems with pressurizing. Therefore, CO<sub>2</sub> is removed by two flash vessels.

To summarize, the presence of CO<sub>2</sub>, even in small amounts, raises problems and results in additional equipment.

### 14.5.3 Extractive distillation solvent

The solvent of choice for extractive distillation is phenol. Phenol is flammable, toxic and corrosive. Therefore it is not the best choice. However, from the evaluated solvents phenol was by far the most effective. It should be further investigated, whether there are solvents with similar effectiveness which are less toxic and/or corrosive. The use of phenol requires stainless steel, thus increasing CAPEX.

### 14.5.4 Equipment size

The equipment for a process with this size are relatively small. As was shown by the Sankey diagram in chapter 13, big streams are separated first. Thereby the flows to following separation steps are drastically reduced. The main CO<sub>2</sub> recycle (97%) almost has no pressure drop. Therefore compressor cost are drastically reduced. The economic evaluation backs up this point, with a capital investment (without the regeneration step) of only 33 million dollar.

## 14.6 Optimization

In this paragraph some optimization possibilities regarding the process are discussed. These are not fully evaluated during the project, but might result in a slightly better process.

A heat integrator network was not made for the process. Though, composite curves indicate that this is only partially possible. As a result heaters and coolers are provided by respectively steam or cooling water. Thereby the  $\Delta T$  is in general way bigger than the minimum  $\Delta T$  of 10°C, thus required surface area is drastically reduced.

There are 2 output streams for DMC. The bottom stream of T-2072 and the top of T-2074. DMC is the final product and therefore has a spec (99.8 wt% pure) which must be met. The spec is the same for both output streams. Though, only the spec of the total output of DMC is relevant. It may be worth trying to vary the specs of both output streams, while the final spec is still met, and investigated the energy requirements of the overall process.

It should also be investigated which compounds may or may not end up in the final product. For example it is undesirable to have phenol in the DMC product, due to its toxicity. In the process mainly dehydrating agent ends up in the final product (of the 0.2wt%).

## 14.7 By-products

By-products were not considered in the process, because Bansode et al. and Honda et al. showed very high selectivity of >99% for this reaction. Therefore only minor amounts of these by-products build up in the system or leave the system via the final product. Probably a purge is sufficient to avoid accumulation of these compounds in the system. It could be that additional separation steps are required, mainly in the regeneration section, so loss of valuable compounds can be avoided.

A minor remark is the ratio of by-products presented in literature. This contradicts with maximum possible formation with respect to stoichiometry.

## 14.8 Economics

An economic evaluation is made in chapter 12. First the investment costs are determined by applying the Lang factor method, then the annual costs of the process are determined and finally sensitivity analyses are made. Also an extended evaluation of the economics is given. Here, only the most important conclusions are presented:

- Small equipment results in low capital investment, about \$33,000,000. Regeneration section not included.
- Annual costs are estimated at \$220,000,000. Contribution from purchasing raw materials is 75%.
- The maximum annual profit is \$95,000,000, with the remark that the regeneration is not included in the cost calculation.
- The high price of dehydrating agent makes it absolutely necessary to limit the loss of it during the process. A maximum loss of 1.4% is determined.
- Profitability strongly depends on the price of methanol, the sensitivity is -1.70.
- Investment costs of the regeneration and catalyst replacement are not important factors for the profit, ROI and PBP.

## 14.9 Conclusions

From the technical and economical evaluations, some conclusions can be drawn about this novel production method for DMC. These are given below:

- The use of a dehydrating agent is found to be the best manner to enhance the direct synthesis of DMC from methanol and CO<sub>2</sub>.
- 2-cyanopyridine is selected as most suitable dehydrating agent. Note that regeneration is not proven to be possible within a realistic time period.
- The process is viable when considering the regeneration part as a grey box.
- A high recovery of the dehydrating agent (2-cyanopyridine) is crucial to obtain a profitable process.
- Looking at the Sankey diagram, the process is very efficient in term of equipment size and utility costs.

## 14.10 Recommendations

- Research is needed for the regeneration reaction, 2-picolinamide to 2-cyanopyridine. This process is only applicable if this reaction can be carried out on a large scale.
- Although a lot of dehydrating agents are investigated, there might be a more suitable one available.
- Reactor scale up from the lab scale experiments described in literature to the industrial scale reactor is probably not accurate. Investigation of an intermediate set up is highly recommended.
- The formation of by-products is not taken into account. For further research this should be one of the main topics.
- Catalyst deactivation should be studied, as it quickly loses its activity (40% conversion after 200h).

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## 16 List of symbols

Symbol	Description	SI Units
A	Surface area for heat exchanger	$m^2$
B	Bottom flow distillation column	$\frac{mol}{s}$
Bi	Biot number	-
C	Concentration	$\frac{mol}{m^3}$
$C_0$	Initial concentration	$\frac{mol}{m^3}$
$C_{DR}$	Cost of distributors	\$
$C_P$	Constant pressure heat capacity	$\frac{J}{K * mol}$
$C_B$	Base costs	\$
$C_P$	Cost of major equipment	\$
$c_g$	Concentration in the gas phase	$\frac{mol}{m^3}$
$c_l$	Concentration in the liquid phase	$\frac{mol}{m^3}$
$C_{PK}$	Cost of packing	$\frac{\$}{m^3}$
D	Distillate flow distillation column	$\frac{mol}{s}$
D	Diffusion coefficient	$\frac{m^2}{s}$
$Da_I$	Dahmköhler number 1	-
$Da_{III}$	Dahmköhler number 3	-
$d_{tube}$	Inside tube diameter	m
$dH_{reaction}$	Enthalpy of reaction	$\frac{J}{molDMC}$
D	Diameter flash vessel	
$D_i$	Inner diameter	
E	Weld efficiency	-
ERPG	Danger factor for chemical exposure index	-
F	Flow	$\frac{mol}{s}$
F1	Factor 1 fire and explosion index	-
F2	Factor 2 fire and explosion index	-
$F_D$	Compressor drive factor	-
$F_{in}$	Flow into the vessel	$\frac{m^3}{s}$
$F_{cooling\ water}$	Flow of the cooling water	$\frac{m^3}{s}$
$f_{ft}$	Fouling factor in the tube side of the reactor	$\frac{J}{m^2 * s * K}$
FI	Flow indicator	-
$F_M$	Material factor for price	-
$F_{out,g}$	Flow out of the vessel in the gas phase	$\frac{m^3}{s}$
$F_P$	Pressure factor heat exchanger costing	-

$F_{\text{steam}}$	Steam volume flow	$\frac{m^3}{s}$
$F_L$	Liquid flow rate	$\frac{m^3}{s}$
$f_L$	Lang factor	-
$F_T$	Heat exchanger correction factor (co/counter current)	-
$F_V$	Vapour flow rate	$\frac{m^3}{s}$
FrC	Fraction control	-
$H$	Pump head	m
h	Liquid level	m
$H$	Henry's constant	$\frac{mol * m^2}{kg}$
$h_b$	Level in reboiler accumulator	-
$h_c$	Level in condenser accumulator	-
$h_v$	Height of vessel	m
$I_c$	Chemical engineering cost index, current	-
$I_r$	Chemical engineering cost index, reference	-
$k$	Specific heat ratio	-
$k_{\text{steel}}$	Thermal conductivity of steel	$\frac{J}{m * s * K}$
kL	Mass transfers coefficient	$\frac{m}{s}$
HLSD	High level shut down	-
HTSD	High temperature shut down	-
L	Length of a unit	m
LC	Liquid control	-
LLSD	Low level shut down	-
$l_t$	Length between trays in distillation column	M
$m$	Molar weight	$\frac{g}{mol}$
M	Liquid/gas distribution factor	-
MF	Material factor fire and explosion index	-
MW	Molar weight	$\frac{g}{mol}$
$m$	Mass flow	$\frac{kg}{s}$
NT	Number of tubes	-
$N_T$	Number of trays	-
Nu	Nusselt number	-
P	Pressure	Pa
$P_B$	Base power needed	$\frac{J}{s}$
PC	Pressure control	-
$P_C$	Power consumption	$\frac{J}{s}$
$P_d$	Design pressure	Pa
Pcon	Pressure in the condenser	Pa
Pe	Peclet number	-
$P_{in}$	Pressure into the vessel	Pa
PI	Pressure indicator	-

Pr	Prandtl number	-
Preb	Pressure in the reboiler	Pa
PO	Pressure of operation	Pa
P <sub>out</sub>	Pressure out of the vessel	Pa
P <sub>shel</sub>	Pressure in the shell side of the heat exchanger	Pa
R	Ratio of flow rates times specific heat	-
R	Reflux ratio	-
Re	Reynolds number	-
$r_{eff}$	Effective reaction rate	$\frac{mol}{m^3 * s}$
S	Sensitivity variable	-
S	Maximum allowable stress	Pa
S	Temperature efficiency	-
Sc	Sherwood number	-
P <sub>steam</sub>	Pressure of the steam	Pa
S <sub>high</sub>	Higher boundary size factor	-
S <sub>low</sub>	Lower boundary size factor	-
T	Temperature	K
TC	Temperature control	-
$t_p$	Wall thickness	-
TI	Temperature indicator	-
T <sub>in</sub>	Temperature into the vessel	K
T <sub>out</sub>	Temperature out of the vessel	K
$t_s$	Shell thickness pressure vessel	m
To	Temperature of operation	-
Q	Energy utility	$\frac{J}{s}$
QC	Quality control	-
Q <sub>c</sub>	Condenser duty	$\frac{J}{s}$
Q <sub>h</sub>	Heater duty	$\frac{J}{s}$
Q <sub>min</sub>	Minimum energy utility	$\frac{J}{s}$
Q <sub>min</sub>	Minimum energy utility	$\frac{J}{s}$
U	Heat transfer coefficient	$\frac{J}{m^2 * s * K}$
$u_g$	Gas superficial velocity	$\frac{m}{s}$
$u_l$	Liquid superficial velocity	$\frac{m}{s}$
$u_s$	Settling velocity vertical flash vessel	$\frac{m}{s}$
$u_t$	Settling velocity liquid droplets in flash vessel	$\frac{m}{s}$
$u_v$	Gas velocity in distillation column	$\frac{m}{s}$
V	Molar volume	$\frac{m^3}{mol}$
V <sub>p</sub>	Volume of packing in column	m <sup>3</sup>
W	Weight of vessel	kg

$w_{ff}$	Fouling factor of water	$\frac{J}{m^2 * s * K}$
$V_L$	Liquid volume	$m^3$
$X_b$	Fraction in the bottom of the distillation column	-
$x_f$	Fraction of component into distillation column	-
$\alpha$	Heat transfer coefficient	$\frac{J}{m^2 * s * K}$
$\Delta H_{vap}$	Heat of evaporation	$\frac{J}{mol}$
$\Delta T_{LM}$	Logarithmic temperature difference in heat exchanger	K
$\Delta H_r$	Heat of reaction	$\frac{J}{molDMC}$
$\varepsilon$	Fraction catalyst in the reactor	$\frac{m_{cat}^3}{m_{reactor}^3}$
$\eta$	Dynamic viscosity	$\frac{kg * s}{m}$
$\eta_B$	Efficiency compressor blower	-
$\eta_M$	Efficiency of the motor	-
$\eta_P$	Efficiency of the pump	-
$P_{cat}$	Effective catalyst density	$\frac{kg}{m_{reactor}^3}$
$\rho_L$	Liquid density	$\frac{kg}{m^3}$
$\rho_G$	Gas density	$\frac{kg}{m^3}$
$\Phi$	Mole flow	$\frac{mol}{s}$
$\Phi_G$	Gas volumetric flow rate	$\frac{s}{m^3}$
$\Phi_m$	Mole flow	$\frac{mol}{s}$
$\tau_L$	Residence time of the liquid	s
$\tau_V$	Vapour residence time	s
$T_w$	Wall temperature	K
$\nu$	Kinematic viscosity	$\frac{m^2}{s}$

## Appendix A Original assignment

Bansode et al. investigated the direct synthesis of DMC from methanol and CO<sub>2</sub>. They managed to achieve a high conversion and selectivity in a continuous reactor. This is the first time this was presented. At equilibrium this reaction has only 1% conversion, but Bansode et al. use a dehydrating agent, 2-cyanopyridine, to scavenge the water and push the equilibrium towards DMC. This is schematically shown in Figure 30.[7]

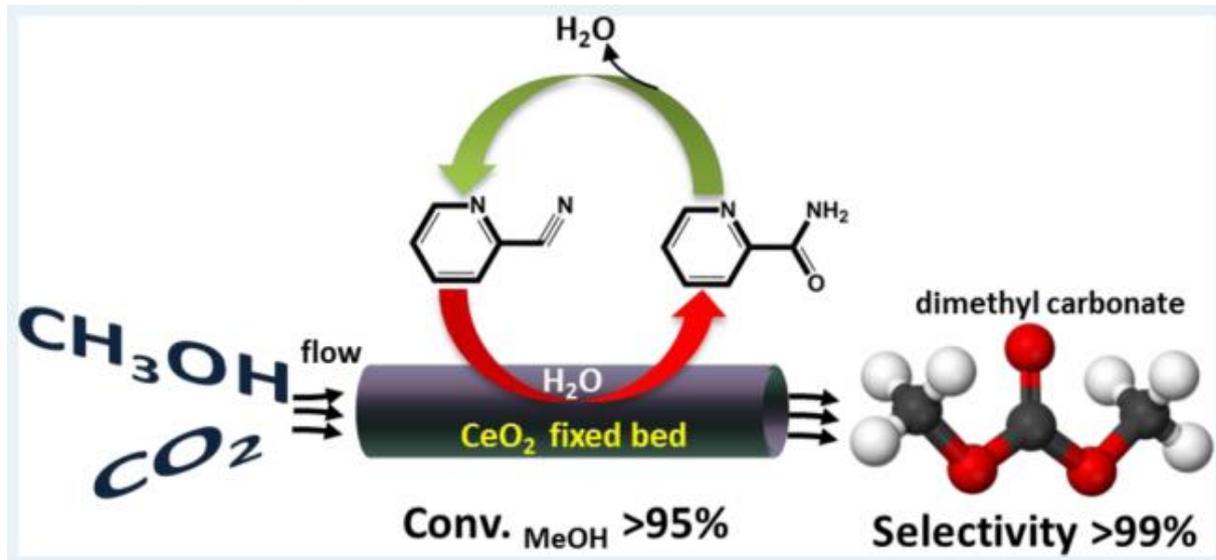


Figure 30: Schematic overview of the reaction[7]

The assignment is to develop an industrial scale plant involving this reaction. Primarily 2-cyanopyridine will be investigated as dehydrating agent, but also other compounds might be considered if there are problems arising with for example the regeneration.

The design of the process has to be carried out in a systematic manner.

## Appendix B Basic Basic data

In this chapter, the physical and chemical properties of the compounds involved are presented. The data includes:

- Specific heat
- Liquid density
- Viscosity
- Boiling point
- Diffusion coefficients
- Vapour-liquid equilibrium

First an overview of the important data is given for the different compounds involved in the system. Then the physical and chemical properties are given. If possible, the effect of temperature is also provided.

### Appendix B.1. Overview of data

The most important physical and chemical properties are given in Table 42. These data are for standard conditions

Table 42: Summary of important physical and chemical properties[48, 49, 71, 84, 86, 87]

Phase	Dimethyl carbonate		Methanol		Carbon dioxide		Water		2-cyanopyridine	2-picolinamide
	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas		
Enthalpy of formation (kJ/mol)	-608.74	-571	-239.5	-205	-	-393.51	-285.83	-241.81	209.97	-156.3
Heat of combustion (kJ/mol)	-	-	-726.5	-763.68	-	-	-	-		
Entropy of formation (J/(mol*K))	-	366.01	126.8	-	-	213.79	69.95	188.8		
Cp (J/(mol*K, 298 K))	30	128.12	81	44.06	-	37.12	75.38	33.59		
Boiling point (K, 1 bar)	363.15	363.15	337.8	337.8	-	-	373.15	273.15	486	557
Melting point (K, 1 bar)	274.15	274.15	175.35	175.35	216.55	216.55	273.15	273.15	300	383
Enthalpy of vaporisation (kJ/mol)	37.7	37.7	35.25	35.25	-	-	44	44		
MW (g/mol)	90	90	32	32	44	44	18	18		
Density (g/cm <sup>3</sup> , 298K)	1.06	-	0.79	-	-	-	1	-		
Price (\$/mt)	700	700	500	500	5	5	0.15	0.15	9150	

## Appendix B.2. Specific heat

The specific heat is an important property and is also used to calculate the enthalpy and entropy at different temperatures. Table 43 gives the constants to calculate the specific heat, enthalpy and entropy for carbon dioxide, water and carbon monoxide (a possible side product). The equations used for this are given below.

$$C_p = A + Bt + Ct^2 + Dt^3 + \frac{E}{t^2} \quad (\text{B.1})$$

$$H - H_{298} = At + B\frac{t^2}{2} + C\frac{t^3}{3} + D\frac{t^4}{4} - \frac{E}{t} + F - H \quad (\text{B.2})$$

$$S = A \ln t + Bt + C\frac{t^2}{2} + D\frac{t^3}{3} - \frac{E}{2t^2} + G \quad (\text{B.3})$$

$$t = \frac{T}{1000} \quad (\text{B.4})$$

Table 43: Constants for the determination of the specific heat, enthalpy and entropy.  $P = 1 \text{ bar}$ . [71]

Compound	Carbon dioxide		Water			Carbon monoxide	
	Gas		gas	liquid	Gas		
T <sub>range</sub> (K)	298. - 1200.	1200. - 6000.	500. - 1700.	1700. - 6000.	298. - 500.	298. - 1300.	1300. - 6000.
A	25.00	58.17	30.09	41.96	-203.61	25.57	35.15
B	55.19	2.72	6.83	8.62	1523.29	6.10	1.30
C	-33.69	-0.49	6.79	-1.50	-3196.41	4.05	-0.21
D	7.95	0.04	-2.53	0.10	2474.46	-2.67	0.01
E	-0.14	-6.45	0.08	-11.16	3.86	0.13	-3.28
F	-403.61	-425.92	-250.88	-272.18	-256.55	-118.01	-127.84
G	228.24	263.61	223.40	219.78	-488.72	227.37	231.71
H	-393.52	-393.52	-241.83	-241.83	-285.83	-110.53	-110.53

The reactor is operating at 30 bar, therefore the specific heat at that pressure is also interesting. A fit from data points is made for water and carbon dioxide. This is shown in Figure 31 and Figure 32 respectively.

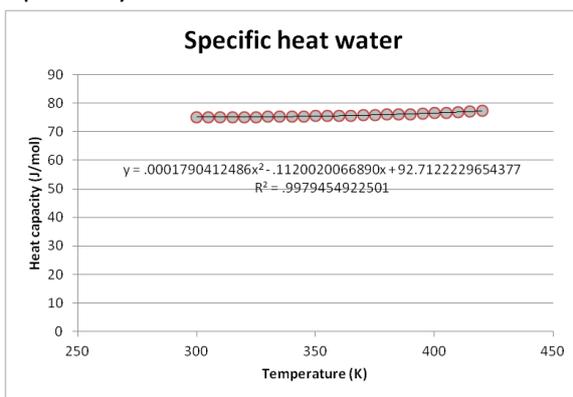


Figure 31: Specific heat of water at 30 bar [71]

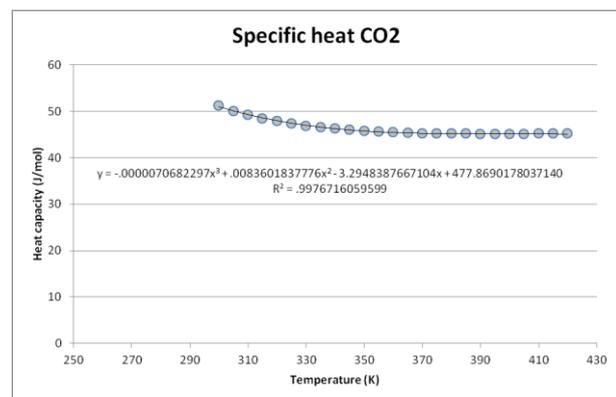


Figure 32: Specific heat of carbon dioxide at 30 bar [71]

For methanol, DMC, 2-cyanopyrdine and 2-picolinamide a different approach is taken. Here the values at different temperatures are known and a polynomial it is made. The methanol specific heat is given in Figure 33 and Figure 34.

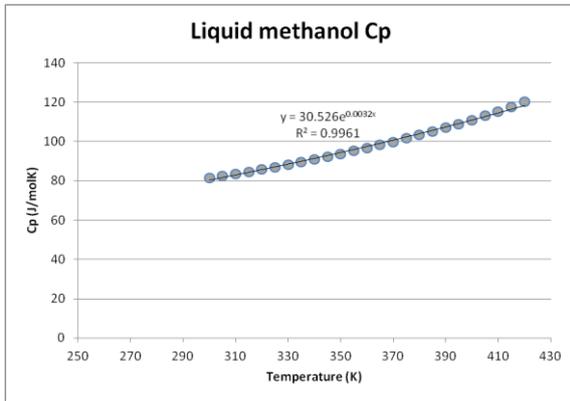


Figure 33: Specific heat of methanol at 30 bar[71]

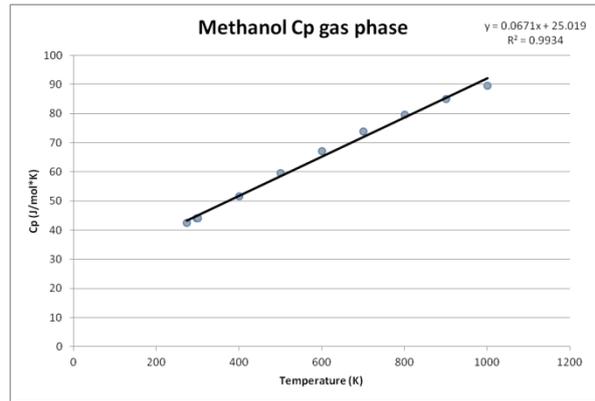


Figure 34: Specific heat of gas phase methanol at 1 bar[71]

The DMC specific heat can be found in Figure 35 and Figure 36.

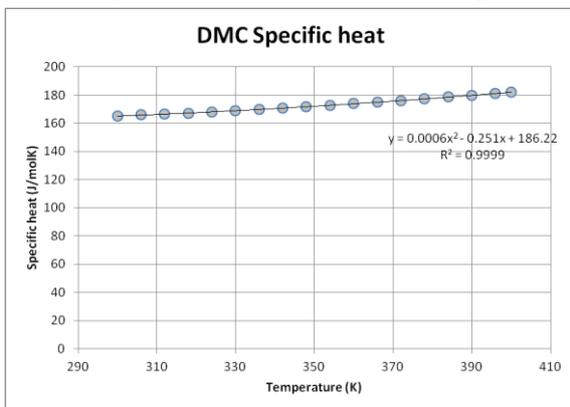


Figure 35: DMC specific heat at 10 bar[71]

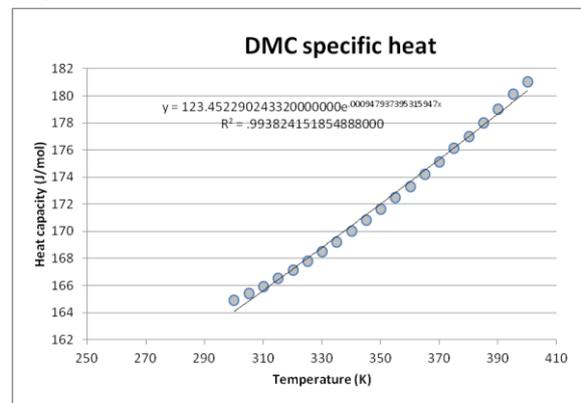


Figure 36: DMC specific heat at 30 bar[71]

Also data for 2-cyanopyridine and 2-picolinamide is available. These graphs can be found in respectively Figure 37 and Figure 38.

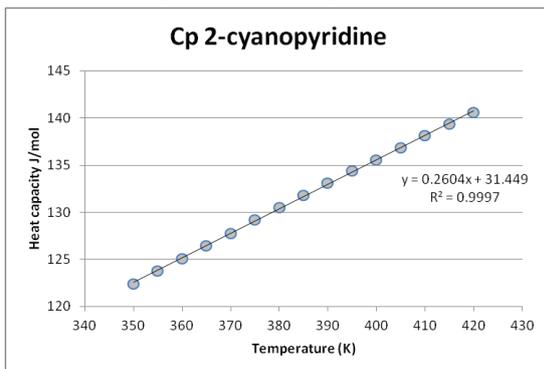


Figure 37: Specific heat of 2-cyanopyridine at 1 bar

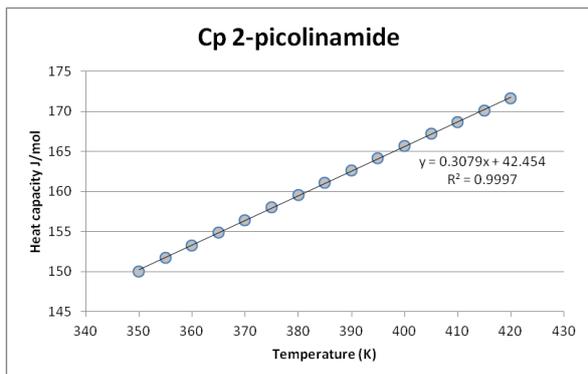


Figure 38: Specific heat of 2-picolinamide at 1 bar

### Appendix B.3. Density

The liquid density of the compounds in the process is needed at different temperature. As CO<sub>2</sub> is always in the gas phase, the density of this is not needed, but can be calculated with an EOS.

Fits of experimental data is given for water (Figure 39), methanol (Figure 40), DMC (Figure 41), 2-cyanopyridine (Figure 42) and 2-picolinamide (Figure 43).

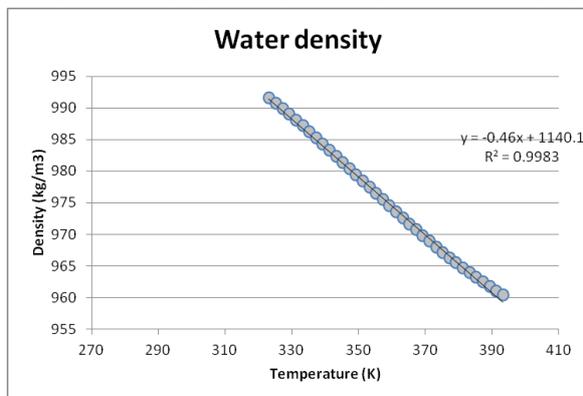


Figure 39: Water density[71]

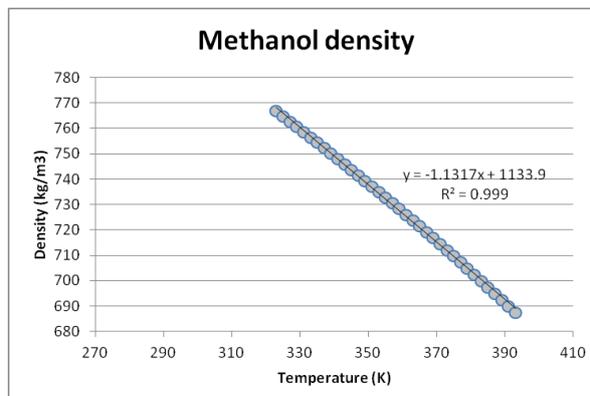


Figure 40: Methanol density[71]

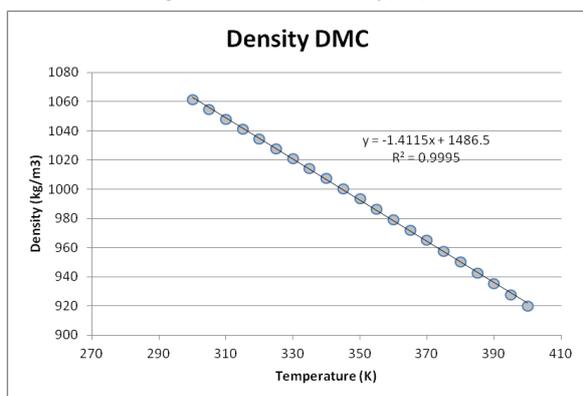


Figure 41: DMC density[71]

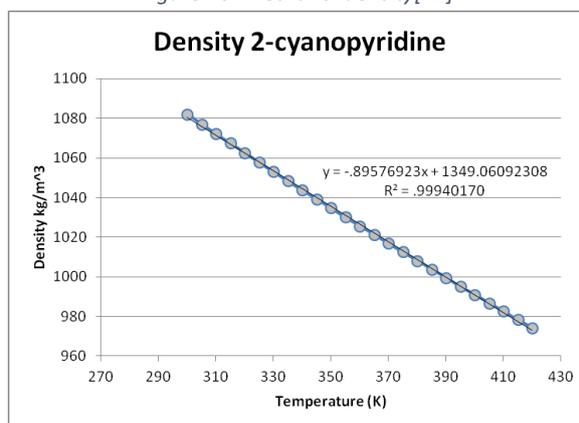


Figure 42: 2-cyanopyridine density[71]

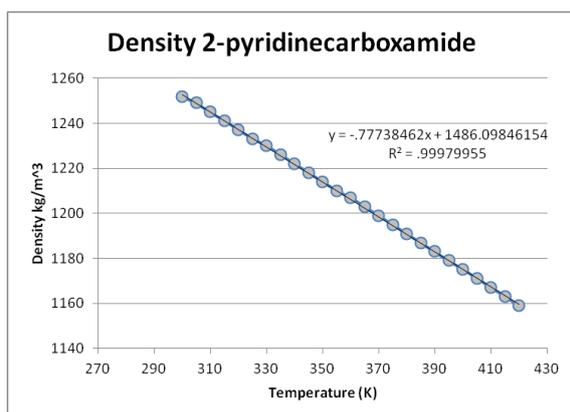


Figure 43: 2-picolinamide density[71]

## Appendix B.4. Viscosity

The viscosities of the compounds involved in the process are given in this section. These can be found in Figure 44 until Figure 48. Only for liquid DMC and 2-picolinamide, no viscosity as function of temperature is found.

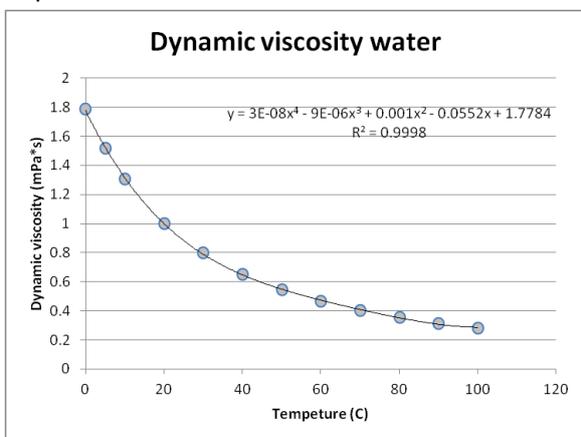


Figure 44: Dynamic viscosity of liquid water[71]

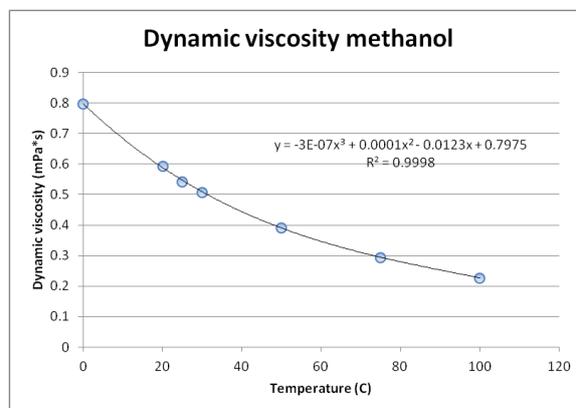


Figure 45: Dynamic viscosity of liquid methanol[71]

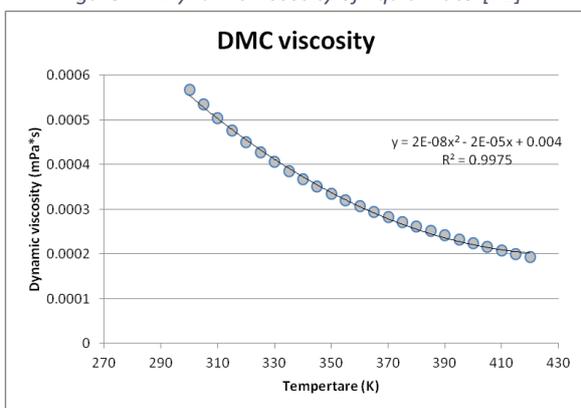


Figure 46: Dynamic viscosity of gaseous DMC[71]

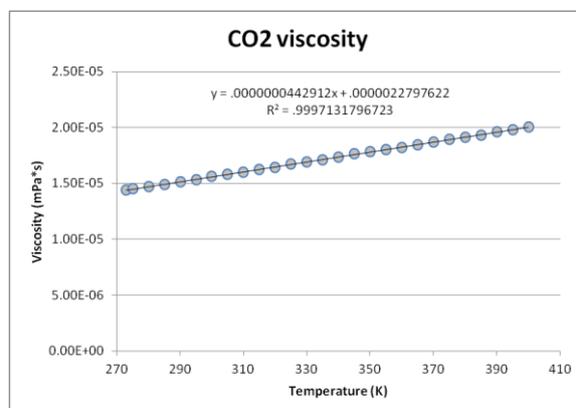


Figure 47: Dynamic viscosity of gaseous CO<sub>2</sub>[71]

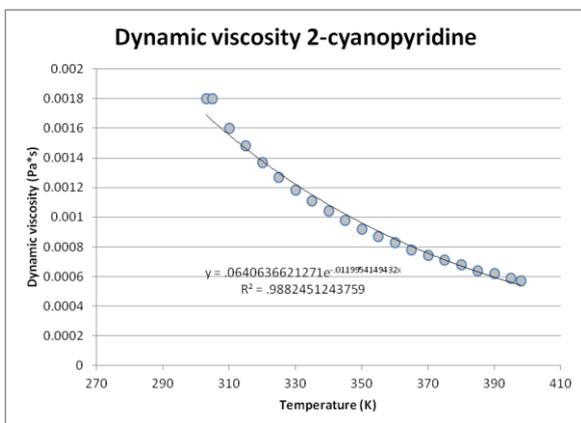


Figure 48: Dynamic viscosity of liquid 2-cyanopyridine[71]

## Appendix B.5. Boiling point

In order to find out the phases of the components at the operating pressures, it is useful to know the boiling point of the components at a range of pressures. This is needed for water, methanol and DMC. Figure 49, Figure 50 and Figure 51 shows the boiling point as function of pressure.

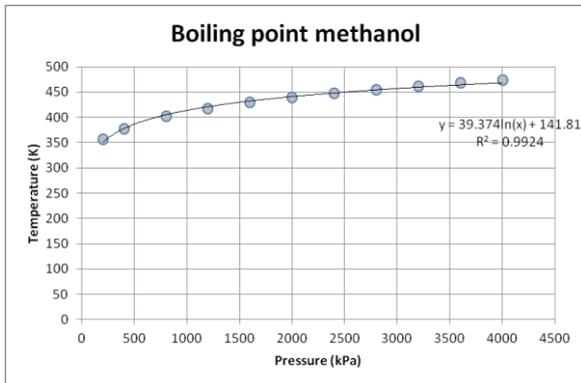


Figure 49: Boiling point of methanol as function of pressure[71]

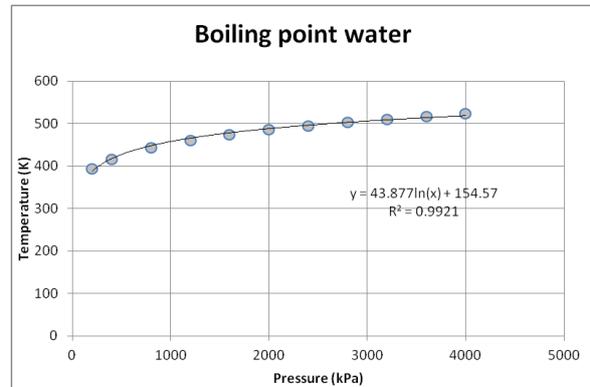


Figure 50: Boiling point of water as function of pressure[71]

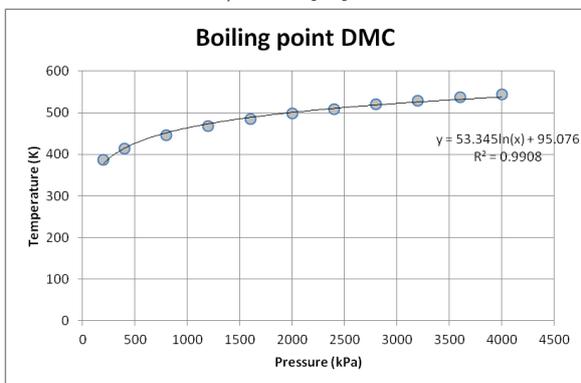


Figure 51: Boiling point of DMC as function of pressure[71]

## Appendix B.6. Diffusion coefficients

The diffusion coefficients of the variety of components were estimated with the Wilke-Chang correlation:

$$D = 7.4 * 10^{-8} * \frac{T * M_W^{0.5}}{V^{0.6} * \eta} \quad (B.5)$$

For this the T is the temperature, the M the molar mass of the compound that is diffused in and the viscosity is also for this component. The molar volume is for the compounds that diffuse through the other medium.

## Appendix B.7. VLE-data

Vapour-liquid equilibrium data is important for the separation of methanol and DMC. In literature the VLE data is available and Figure 52 gives the x,y-diagram. This can be used to validate UNISIM simulations models.

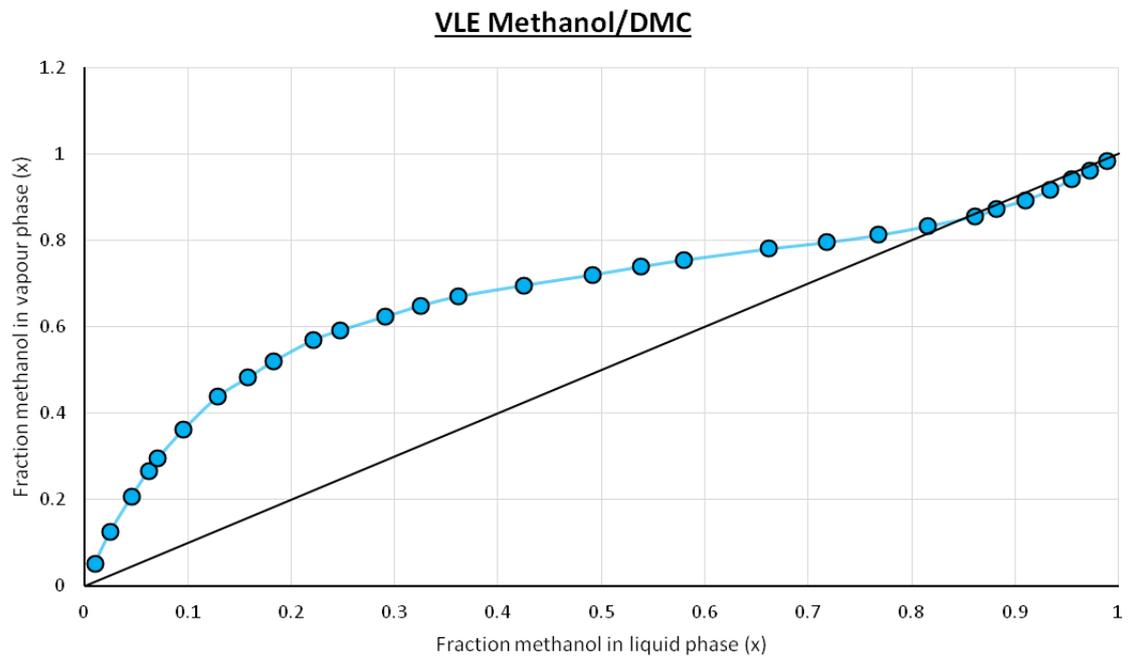


Figure 52: VLE- data of a methanol and DMC mixture, from Rodriguez et al. [61]

## Appendix C Chapter 2 - Process information

### Appendix C.1. PFD's current employed technologies

The Appendix shows the PFD's and block diagrams of the production technologies which are discussed in the introduction of this report, starting with the oxidative carbonilation route.

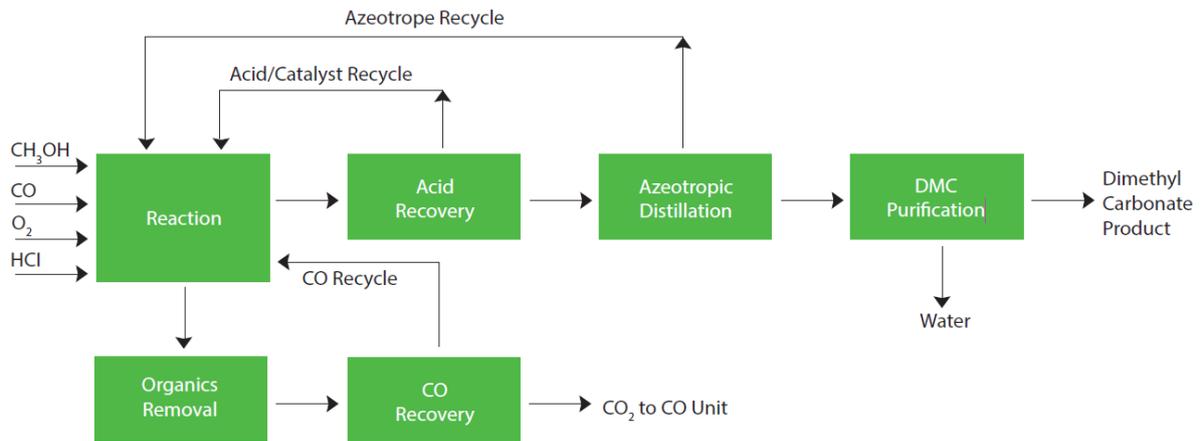


Figure 53: Block diagram oxidative carbonilation route. From: [26]

Ube's nitric oxide route:

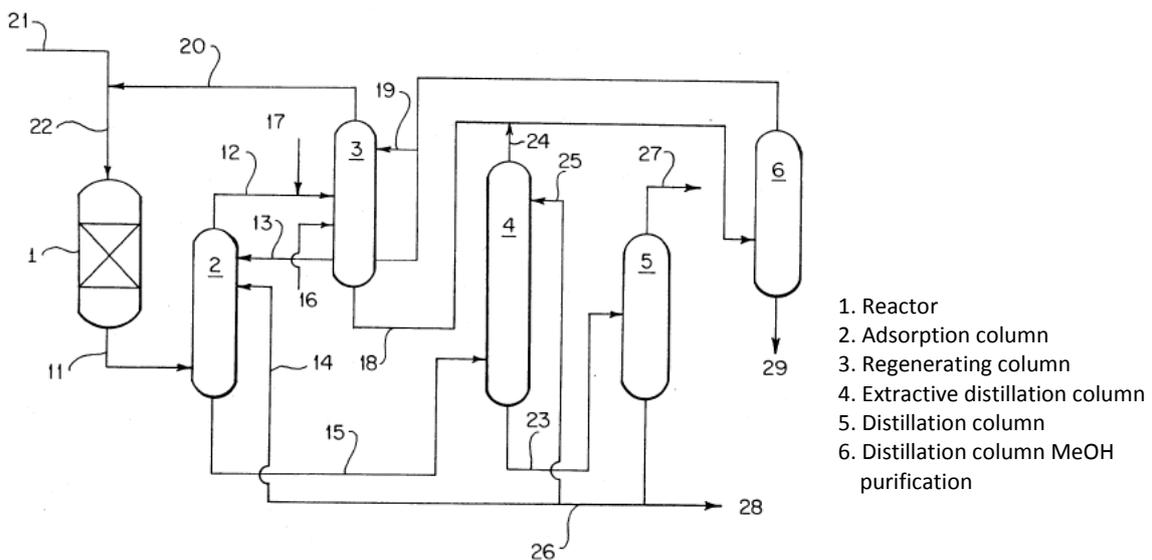


Figure 54: Ube's nitric oxide route for the production of DMC. Adapted from: [88]

## Appendix C.2. Enhancement of the conversion

The removal of water from the reactor is one of the options that could be applied to enhance the reaction. An overview of these option is provided in Figure 55 and briefly discussed below.

### C.2.1. Concepts to remove water

#### C.2.1.1. Membrane reactor

A membrane catalytic reactor (MCR) can be used to separate the water which will be formed during the reaction. Li et al. described this process with three kinds of supported membranes; silica inorganic membrane (S), polyimide-silica (PS) and polyimide-titania hybrid membrane (PT). The catalyst is copper supported by MgO-SiO<sub>2</sub>. Results are given in Table 44. So, a membrane implemented inside the reactor will increase the conversion and a high selectivity towards DMC remains. [32]

Table 44: Performance of a membrane catalytic reactor with different membrane materials

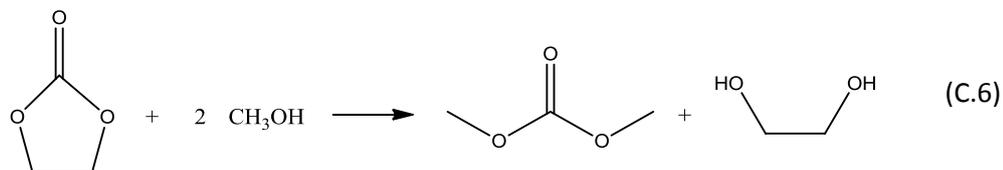
Membrane type	Temperature (°C)	Pressure (bar)	Conversion	Selectivity
P	120	40	8.1	91.4
PS	130	40	9.2	96.0
PT	130	40	8.9	93.3

#### C.2.1.2. Molecular sieve

Molecular sieves can take up some of the water generated during the reaction, so it is some sort of dehydrating agent, but the reactor system described is different than in the conventional way. The molecular sieve used in the research is zeolite 3A. Optimal operating temperature for the adsorption of water on this molecular sieve is room temperature, were the reaction must be carried out at much higher temperatures. Therefore the adsorber with zeolite 3A is separated from the main reactor. Some part of the reaction mixture is continuously circulated through the molecular sieves. So, this has to be cooled down and heated up again. In literature this is described by Choi et al. and a conversion of nearly 50% is reached. However the reaction time is very long, about 75h. Although the influence of some variables (e.g. circulation flow) is not discussed, it probably is not suitable for large scale operation. [37, 56]

#### C.2.1.3. Reactive distillation

Reactive distillation might be an option to separate the products DMC and water. If this can be carried out successfully, then no other separations steps are needed. The production of DMC using reactive distillation is primarily investigated using another route [57, 68, 89, 90]:



In this case propylene glycol is used instead of CO<sub>2</sub> as a reactant. This is done to avoid gas phase reactions in the distillation column. No research has been found for doing this reaction using CO<sub>2</sub>. Besides, no water is formed in the reaction using propylene glycol, this would also complicate the process. It is not possible to use reactive distillation with methanol and CO<sub>2</sub> as reactant. In this situation, both reactants leave the column at the top and the products leave the column at the bottom.

#### C.2.1.4. Dehydrating agents

Dehydrating agents are used to react with water and therefore shift the equilibrium towards the product side of the reaction. Different kinds of dehydrating agent are used in literature and an overview is given below. The co-author of the article about 2-cyanopyridine (M. Tamura) is contacted to obtain more information about potential dehydrating agents. In addition the information specialist of the Faculty of Science and Technology of the Twente University (H. Becht) is contacted several times to deepen the literature research on potential dehydrating agents.

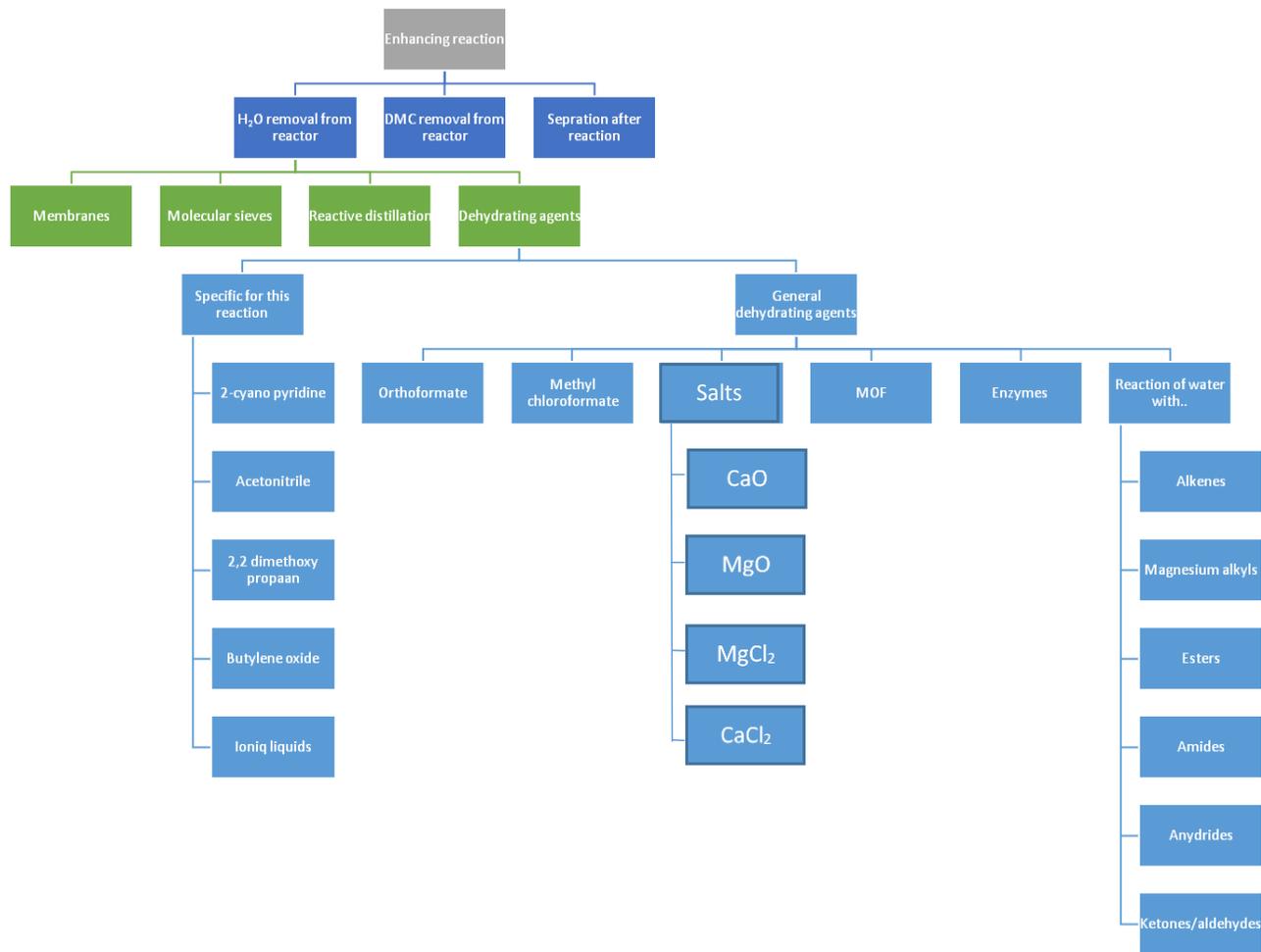


Figure 55: Overview of dehydrating agents

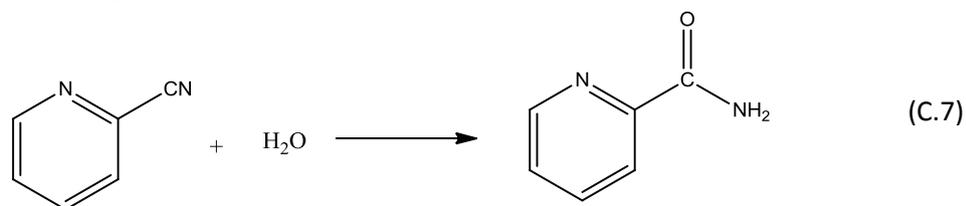
### C.2.1.4.1. 2-cyanopyridine

Different nitriles as dehydrating agents have been reported by Honda et al. and the yields are given in Figure 56. From this study 2-cyanopyridine is selected as best dehydrating agent for this reaction, giving 2-picolinamide as final product [6, 7]. However, this 2-picolinamide has to be regenerated to 2-cyanopyridine and this is reported to be possible, but the way to do this is not explained.[7]

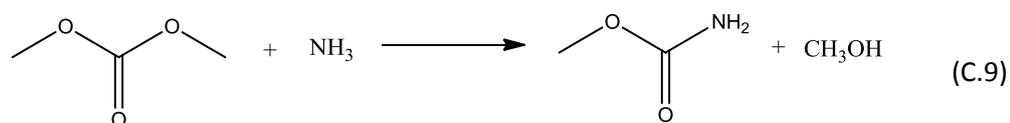
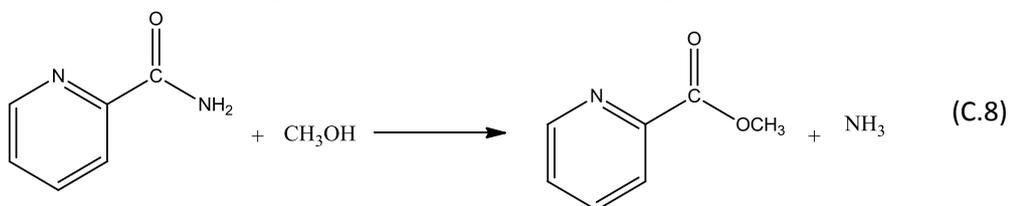
Entry	Nitrile	Yield of products [%] <sup>[a]</sup>			
		DMC	methyl carbamate	amide	ester
1		94.0	0.99	94.6	1.18
2		91.2 <sup>[b]</sup>	0.18 <sup>[b]</sup>	86.9 <sup>[b]</sup>	0.26 <sup>[b]</sup>
3		38.6 <sup>[b]</sup>	0.41 <sup>[b]</sup>	44.1 <sup>[b]</sup>	0.69 <sup>[b]</sup>
4		2.06	n.d.	3.06	<0.1
5		4.10	n.d.	2.72	0.20
6		2.94	n.d.	4.74	n.d.
7		n.d.	n.d.	<0.1	<0.1
8	$\text{H}_3\text{C}-\text{CN}$	0.38	<0.1	0.48	<0.1
9		0.76	<0.1	0.74	<0.1
10	none	0.32	-	-	-

Figure 56: Yields of different dehydration agents; the amide refers to 2-picolinamide and the ester and methyl carbamate are formed as by-products[6]

The reaction equation is given below:



Methyl carbamate and the formation of an ester are reported as by-products. However, the selectivity is quite high. The side-reactions are given in equations (C.8) and (C.9)[6].



A major advantage of the combination with this dehydration agent is the catalyst [6, 7]. The dehydration reaction can also be catalysed with cerium oxide. Probably this is the reason why cerium oxide is chosen as catalyst in this system.

The reaction mechanism is shown in Figure 57, with cerium oxide as catalyst for both the DMC synthesis and dehydration reaction [31].

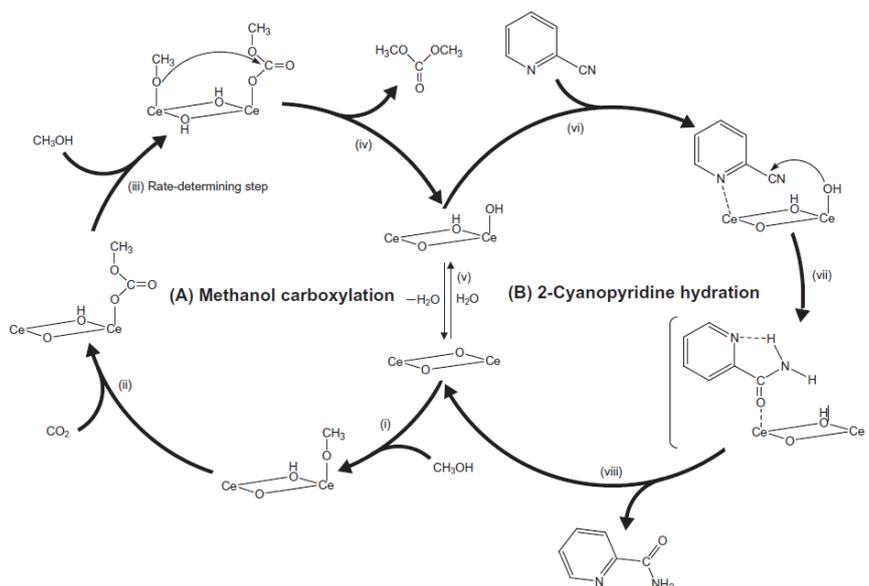
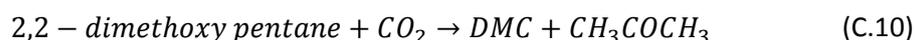


Figure 57: Reaction mechanism of the direct synthesis of DMC with 2-cyanopyridine as dehydrating agent with ceria as catalyst[31]

#### C.2.1.4.2. 2,2-dimethoxy propane (DMP)

DMP is a dehydrating agent that works different than 2-cyanopyridine. Here the water is 'removed' before the DMC is formed. Starting product is not methanol, but DMP. This DMP reacts with  $\text{CO}_2$  to form DMC and acetone (eq.(C.10)). Methanol is used to convert the acetone back to DMP and also produces the water (eq.(C.11)). Pretty high conversions can be obtained, up to 56%, but the time to reach this conversion is similar to that of the molecular sieves ( $\pm 75\text{h}$ ). [91-94]



#### C.2.1.4.3. Acetonitrile

Before cyanopyridines became interesting as dehydrating agent, reports of acetonitrile were published [6, 95]. Acetonitrile is able to react with water and form acetamide. For the reacting to DMC, no conversion is reported, but the same synthesis was carried out for diethyl carbonate and dipropylcarbonate. Here the conversion is 42% and 33% respectively.[95, 96]

#### C.2.1.4.4. Butylene oxide

Butylene oxide can be used as dehydrating agent. The conversion of the butylenes oxide is reported to be very high, but no stoichiometric ratio is used between the dehydrating agent and methanol. Therefore the conversion of methanol is enhanced, but not extremely high. A big disadvantage of butylenes oxide is the selectivity of DMC calculated from methanol. This drops dramatically compared to the cases without dehydrating agent.[97, 98]

#### C.2.1.4.5. Ionic liquids

Eta et al. tried a different approach with ionic liquids to trap the water from the reaction mixture. The anion in the ionic liquids is a methoxide and the cations used are imidazolium with different side groups. In this way the conversion is increased up to 12.6%, but the selectivity towards DMC drops below 90% or even to 69%. Regeneration of the dehydrating agent is possible and will slightly deactivate the ionic liquid.[99]

#### C.2.1.4.6. Summary

The addition of a dehydrating agent will shift the equilibrium towards the product side. In literature the effect of a lot of different dehydrating agents are reported. Only 2-cyanopyridine and related compounds are able to reach a very high conversion, without having troubles with the selectivity. As a second option 2,2-dimethoxy pentane could be used.

#### C.2.1.5. Selection

There are four options for the removal of water from the reaction mixture, a membrane reactor, molecular sieves, reactive distillation and the use of a dehydrating agent. A membrane reactor can enhance the reaction a bit and achieve a conversion near 10%. Already a 10x increase compared to the equilibrium conversion. Molecular sieves has a major disadvantage, because the optimal adsorption conditions do not overlap with the conditions during the DMC synthesis. Therefore an internal recycle is needed. The conversion is acceptably high, but the time it takes is too long. Reactive distillation is not proven to work with the use of CO<sub>2</sub> as a reactant. Dehydrating agents, especially 2-cyanopyridine, can significantly improve the conversion. Up to 95% is reported, with the selectivity kept above 90%. Therefore a dehydrating agent is found most suitable to enhance the reaction.

Bansode et al. successfully demonstrated the direct conversion of CO<sub>2</sub> and methanol to DMC with a conversion of >95% and a selectivity of 99% in a fixed bed reactor using 2-cyanopyridine as dehydrating agent [7]. However, 2-cyanopyridine should be recovered to create a sustainable process. The recovery of 2-picolinamide back to 2-cyanopyridine results in a problem, it takes a very long time for the reaction to complete.[6]

Recovery of 2-picolinamide to 2-cyanopyridine for 90% takes 400 hours over a NaO/SiO catalyst[6]. Zhou et al. [39] and Sueoka et al. [38] report that recovery with high yields of similar compounds as 2-picolinamide, for example benzamide, is possible in a time span of 24h or less. A vanadium oxide catalyst was used in the study of Sueoka et al., Zhou et al. used relatively cheap iron complexes as catalyst. These studies are done on lab scale and focus on getting a high yield and not on retrieving kinetic constants. Therefore no real estimation on the feasibility of the recovery can be done. However, the time span needed in the latter two studies is way smaller than the 400 hours reported by Honda et al. [6].

A second disadvantage of this dehydrating agent is that the reacted dehydrating agent (2-picolinamide) has a high melting point, namely 105°C. To avoid problems with solid in the reactor and piping, the operation conditions are limited.

Further research is needed to make the direct conversion of CO<sub>2</sub> and methanol to DMC with the use of 2-cyanopyridine feasible. Research about faster and/or more effective ways of 2-picolinamide recovery to 2-cyanopyridine should be conducted.

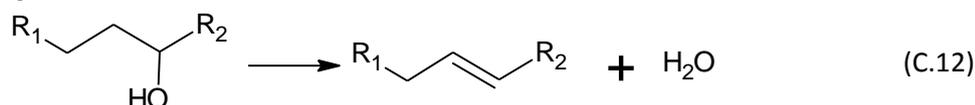
### C.2.2. General dehydrating agents

The current methods to remove water from the reaction mixture described in literature all have major issues. Which raises the need for new methods to remove the water. In the paragraphs C.2.2.1 to C.2.2.6 reactions with water as reactant are listed. In paragraph C.2.2.7 an evaluation of these methods can be found. The use of formats, salts, enzymes and metal organic frameworks (MOFs) are also discussed.

#### C.2.2.1. Organic compounds

##### C.2.2.1.1. Dehydration of alcohols to alkenes

Catalysed by an acid, e.g. sulphuric acid, it is possible to dehydrate alcohols to alkenes. This is a reversible reaction, so it should also be possible to hydrate alkenes to alcohols. Dehydrating of tertiary alcohols is the easiest, because it has the most stable carbocations. Primary alcohols are the hardest to dehydrate.[41]

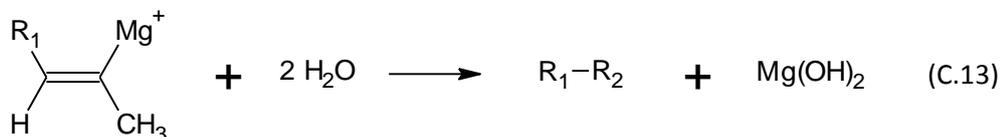


The reaction is reversible so the alkene can be used to remove water. The selectivity during regeneration might be an issue. In most cases, there is a possibility that there are more alkenes possible. This should be chosen very carefully.

In this reaction the alkene is the dehydrating agent and can be regenerated from the alcohol pretty easy. Reactive distillation is mentioned as a suitable method for regeneration. This catalyst will cause problems in the hydration of the alkene. Most common is sulphuric acid, a homogeneous catalyst. A next separation step is therefore needed to regenerate the catalyst. The alkene must be chosen very carefully to avoid selectivity issue in the regeneration.[41]

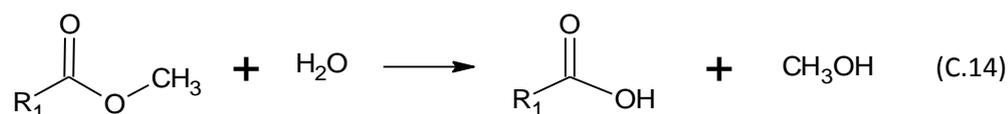
##### C.2.2.1.2. Reaction with magnesium alkyls

Magnesium alkyls are known to react very fast with water. The reaction equation is shown in equation(C.13).[42]



##### C.2.2.1.3. Hydrolysis of an ester

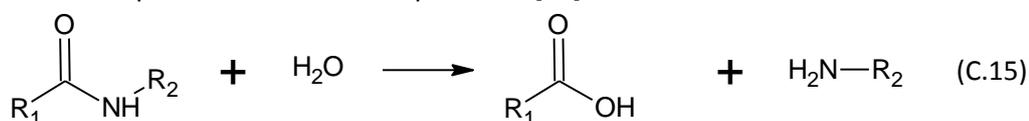
An interesting reaction mechanism involving water is hydrolysis. This is the use of water to split one compound into two other compounds. Esters can be hydrolyzed to obtain an alcohol and an acid. Interesting in this is that it might be possible to obtain methanol as a product. As methanol is obtained as a product after the hydrolysis, the concentration methanol in the reactor will stay constant. This is favourable for the DMC synthesis, but shifts the equilibrium of the hydrolysis reaction to the left. This reaction is catalyzed by hydrochloric acid.[41]



Problems can occur in the equilibrium. Some methods are reported to shift the equilibrium to the right. This is to use an excess of water or by reactive distillation to remove the alcohol. An excess of water is not possible, the only water available is from the DMC synthesis. This is in very small amounts due to the equilibrium. The implementation of this combined with the synthesis of DMC can be a problem.[41]

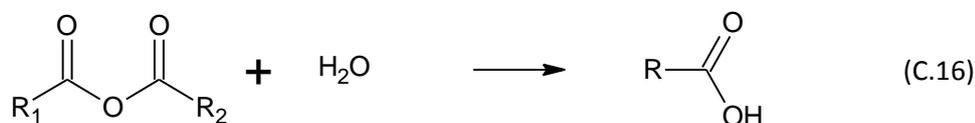
#### C.2.2.1.4. Amide hydrolysis

The same kind of reaction as with an ester, the reaction can also be carried out with an amide. The reaction mixture is heated up and catalysed with hydrochloric acid. Another possibility is to hydrolyze it under very basic conditions. At elevated temperatures the hydration reaction is favoured, the regeneration should be possible at a lower temperature. [41]



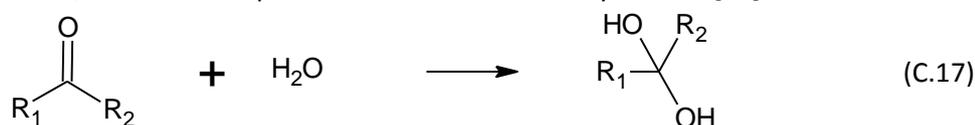
#### C.2.2.1.5. Reaction with an anhydride

Anhydrides are formed when two carboxylic acids are combined with the loss of water. The opposite reaction is desired to remove the water from the reaction mixture. If the alkyl groups of the anhydride are the same, than the product is one single compound. The reaction can go either way, so regeneration is not a problem.[41]



#### C.2.2.1.6. Hydrate formation from ketone or aldehyde

Aldehydes and ketones will react with water to form a hydrate, a molecule with two hydroxide groups bonded to the same carbon. Also this reaction is catalysed with an acid to increase the reaction rate. The equilibrium strongly depends on the groups attached to the carbonyl. For example acetone only has 0.2% conversion in equilibrium, whereas formaldehyde reaches 99.9% conversion. Regeneration is possible in this case, but it does depend on the ketone or aldehyde used.[41]



#### C.2.2.2. Summary

In this section some reactions that use water as reactant are listed. These are all not mentioned in literature in combination with the direct synthesis of DMC. From the list, some of the options are simply not possible. Magnesium alkyls react very fast and regeneration is barely possible, whereas the hydrolysis of esters and amide need an excess of water to overcome problems in equilibrium or need other methods not compatible with the DMC synthesis.

For the hydration of alkenes to alcohols the regeneration can be controlled by temperature. A low temperature favours the hydration and at high temperatures the regeneration. Also anhydrides might be an option. Regeneration is possible, due to the reversibility of the reaction. The same holds for hydrate formation. Here the kind of ketone or aldehyde determines the equilibrium in the reaction. In order to conclude whether these compounds are suitable as dehydrating agent for the DMC synthesis the compatibility with this synthesis should be further investigated. Issues such as the acidic catalyst and the optimal reaction conditions need to be figured out.

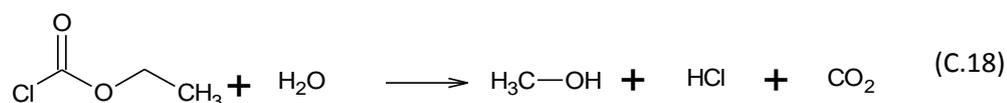
Additional, the selectivity towards water needs to be investigated. It is possible that methanol will also react with a lot of the compounds mentioned. The hydroxyl group is the functional group here and this is present in either water and methanol. Because methanol is much more present in the reactor than water, a very high selectivity towards water need to be achieved.

#### C.2.2.3. *Formates*

An organic chemist (Dr. Willem Verboom) was consulted, who advised to consider the next two formates:

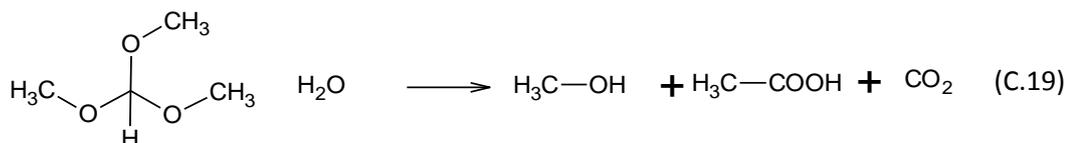
##### C.2.2.3.1. Methyl chloroformate

An example of an ester that could be used as dehydrating agent is methyl chloroformate (the reaction is shown in equation (C.18)). The formation of methanol and CO<sub>2</sub> is interesting. However, it is unknown if this reaction is an equilibrium reaction. On the other hand, using this dehydrating agent does not fit in the idea of using methanol and CO<sub>2</sub> from 'sustainable' sources. Then the focus of the project should be on the sustainable production of the dehydrating agent. Besides, the use of chloride compounds is not very sustainable.



##### C.2.2.3.2. Trimethylorthoformate

Trimethylorthoformate is an ether, which also can react with water, forming methanol, CO<sub>2</sub> and formic acid (as shown in equation (C.19)). The considerations are the same as those given for chloroformate.



#### C.2.2.4. *Salt*

During lab scale synthesis experiments, salts (like magnesium chloride) are sometimes used to dry a mixture. A literature study was performed, which resulted in the next following salts as potential dehydrating agents.

##### C.2.2.4.1. Calcium oxide

Calcium oxide can be used to extract the water from the reaction mixture. This reaction is proposed by Schaube et al. to chemically store excess energy [44]. It dehydrates again at temperatures of 400-500°C when flushed with nitrogen. The big drawback of this is the high temperature needed for dehydration of the compound.

#### C.2.2.4.1.1. Calcium oxide reaction

Calcium oxide, CaO, is an interesting option as a dehydration agent. It reacts with water according to equation (C.20). The Gibbs free energy of reaction at 120°C is -51.1kJ/mol (calculated from data of Barin & Knacke [100]). It was successfully shown by Schaube et al. that full conversion for dehydration and rehydration of this reaction can be achieved in multiple consecutive cycles (at least 25) [44].



#### C.2.2.4.1.2. Overall reaction

The reaction to form DMC from methanol and CO<sub>2</sub> has a Gibbs free energy of +26kJ/mol [97]. As a result, the Gibbs free energy of the overall reaction is negative. Therefore, the overall reaction proceeds at standard conditions, see equation (C.21).



#### C.2.2.4.1.3. Calcium oxide reaction with CO<sub>2</sub>

Besides reacting with water, calcium oxide can also react with CO<sub>2</sub> (see equation (C.22)). The Gibbs free energy of reaction at 120°C is -117.5kJ/mol (calculated from data of Barin & Knacke [100]). This is even much more than the reaction with water. One of the reactants of the main reaction is CO<sub>2</sub> and the partial pressure of water in the reactor is very low due to the low equilibrium conversion, which makes it even more unsuitable. In addition, usually CO<sub>2</sub> is used in excess for the reaction. It is also in agreement with literature. According to Dou et al. water even enhances the uptake of CO<sub>2</sub> [101].



#### C.2.2.4.1.4. Calcium oxide Conclusion

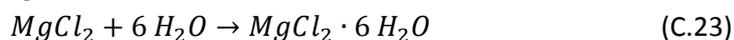
Calcium oxide is not suitable as a dehydrating agent for the process. It favours the reaction with CO<sub>2</sub> over the reaction with water. To make matters worse, there is a CO<sub>2</sub> rich atmosphere in the reactor, while the partial pressure of water is very low.

#### C.2.2.4.2. Magnesium Oxide

To be short, for magnesium oxide the same problems were encountered as for calcium oxide. The reaction of MgO with water gives a Gibbs free energy of -23.4kJ/mol at 120°C (calculated from data of Barin & Knacke [100]). The reaction with CO<sub>2</sub> is even more favoured in case of MgO (-763.2kJ/mol, calculated from data of Barin & Knacke [100]) in comparison to CaO. Also in this case the presence of water enhances the uptake of CO<sub>2</sub>, at certain temperatures it is even crucial for the uptake of CO<sub>2</sub> [102].

#### C.2.2.4.3. Magnesium chloride

Magnesium chloride can possibly be used as a drying agent to remove water in situ from the reactor. Advantage of MgCl<sub>2</sub> is that it will not react with CO<sub>2</sub>. The magnesium chloride forms a complex with water at low temperatures and this complex will break at temperatures around 160-200 °C and thus the magnesium chloride can be regenerated [40].



The magnesium is then regenerated by heating with air in 180-200 °C and then with hydrogen chloride at 300 °C to chlorinate the MgO formed in the step before. This is done commercially in the Hydro Norsk Process [40]. The magnesium has various stages of complexes, it will first change into a complex with 4 water, then to 2 water and at last all the water will be removed [103]. MgCl<sub>2</sub> can take 6 water molecules per ion.

Disadvantages are that it is a solid and it is not used as a drying agent on industrial scale as of yet that we know of, also the chloride is corrosive. The major upsides of this drying agent are that it is cheap and it can be regenerated.

Thermodynamic calculations show that it is possible to use MgCl<sub>2</sub> as a dehydrating agent, Gibbs free energy of -25kJ/mol at 0°C. However, the Gibbs free energy is already very positive at 120°C with 215.8kJ/mol. Therefore MgCl<sub>2</sub> is not suitable as a dehydrating agent for this process.

#### C.2.2.4.4. Calcium Chloride

Calcium chloride (CaCl<sub>2</sub>) is a known desiccant for gasses and liquids [104, 105]. Also for CaCl<sub>2</sub> the Gibbs free energy was calculated (by data from [104] and [106]), results are shown in Table 45. Again, the Gibbs free energy at 120°C is not low enough.

Table 45; Gibbs free energy (kJ/mol) for different CaCl<sub>2</sub> hydrates at different temperatures

T (C)	CaCl <sub>2</sub> ·2H <sub>2</sub> O	CaCl <sub>2</sub> ·4H <sub>2</sub> O	CaCl <sub>2</sub> ·6H <sub>2</sub> O
0	-33.9	-74.0	-111.9
60	-13.0	-34.1	-54.2
120	7.1	4.5	1.9

#### C.2.2.4.5. Conclusion salt

While the advantage of this class of compounds in general is their easy recovery, no suitable salts were found to act as a dehydrating agent. CaO and MgO give problems with respect to the CO<sub>2</sub> rich atmosphere in the reactor. MgCl<sub>2</sub> and CaCl<sub>2</sub> are not suitable at a favourable operating temperature of 120°C.

#### C.2.2.5. Metal-Organic frameworks

Metal-organic frameworks (MOF's) are nanoscale cages that selectively can capture molecules. There are different kinds of MOF's and they are reported to be able to adsorb water molecules. For this, the kind of framework is very important. Some also have the ability to adsorb methanol and/or CO<sub>2</sub>. Examples are lithium, copper or zinc based MOF's.[43, 107-109]

An advantage of MOF's is that regeneration is very easy, but this has to be carried out in a semi-continuous process. Adsorption usually takes place around room temperature, where desorption takes place at elevated temperatures.[43] This causes problems in combination with the DMC synthesis, where the temperature is more favourable for desorption.

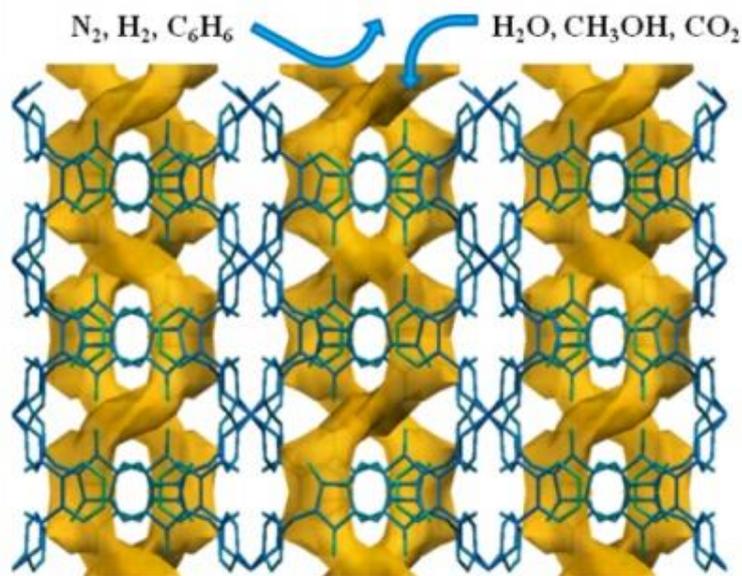


Figure 58: Example of selective capture of a MOF[43]

#### C.2.2.6. Enzymes

Some enzymes are able to convert water into other components. A class of enzymes that is able to convert water and  $\text{CO}_2$  to carbonic acid ( $\text{H}_2\text{CO}_3$ ) are the carbonic anhydrases [110]. This may be interesting to remove water. However, enzymes need a watery environment to function [111]. In addition, they degrade at realistic operating conditions ( $>100^\circ\text{C}$ ). Probably enzymes are too expensive to function as a catalyst for this process.

#### C.2.2.7. Summary

Several options to remove water from the DMC reactor are discussed: reaction with organic compounds and formates, the use of salts, MOFs or enzymes. It is unknown if the reaction with an organic compound is compatible with the DMC syntheses. Also the use of (an acidic) catalyst and the optimal reaction conditions need attention. The use of formates is very interesting, since methanol and  $\text{CO}_2$  are the product of the reaction between the formate and water. Despite of this potential, using this type of dehydrating agent does not agree with the initial goal of the project. At this moment, salts are not industrially used as drying agent, but  $\text{CaO}$  shows potential for this application. For both MOFs and enzymes the operating window do not or barely overlap with the operating window of DMC production.

# Appendix D Chapter 3 - Project organization

## Appendix D.1. Planning

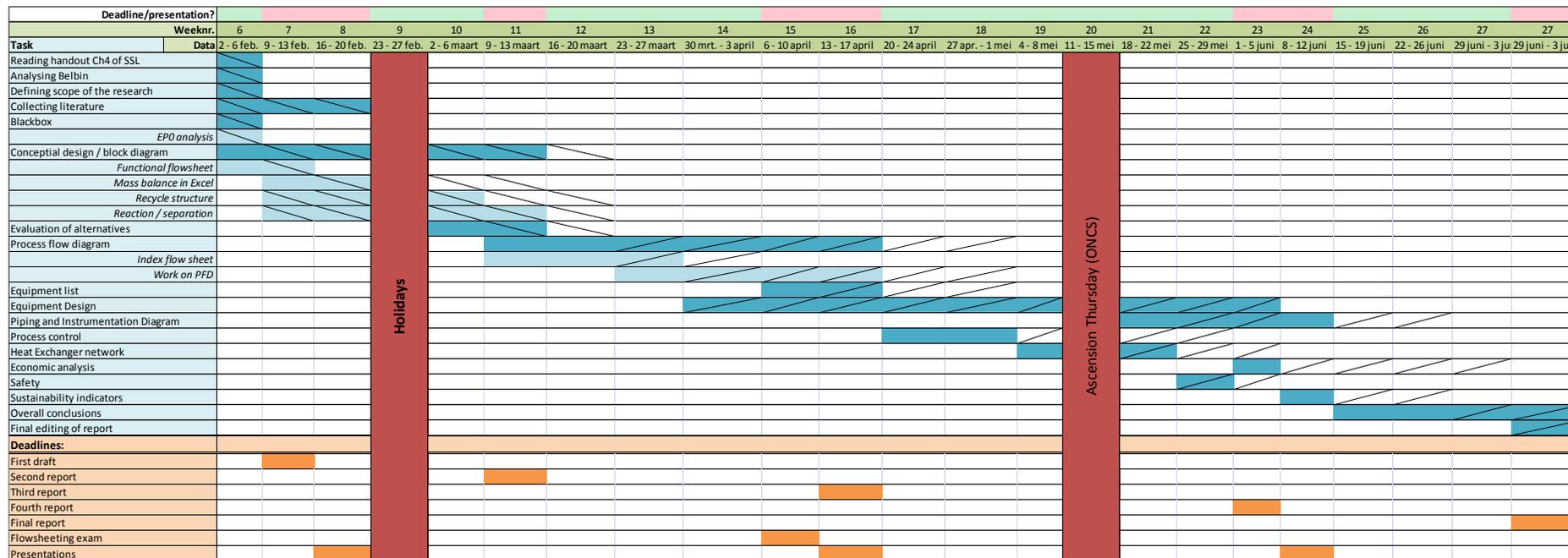


Figure 59: Bar chart planning. Colours indicate the planned period of working at task. Cross indicates the real time spend on task

## Appendix D.2. Project organisation

The hierarchical decision procedure of Douglas is used to organise this project. Initially, this procedure included 5 levels [112], including more details at every level. More levels were added in the past years. The main advantage of this procedure is the generation of alternatives. If one option does not fit in a higher level, it is then possible to step back to the previous level(s) and discuss the other available options. In addition, by documenting all the decisions and alternatives, important decisions might not be overlooked. [112] The design process is started with collecting data about the process that has to be designed and the processes that are already available, this is the first level. By decomposing the flow sheets of existing flow diagrams, it is possible to learn from the operations that are currently done in industry.[81] The different levels are described in more detail below:

### *Level 1: Definition of overall process*

This is done by answering the next kind of questions: Which reactants are used? Which products are produced? Capacity wanted? What are current production methods? Is the process economically feasible (results in  $EP_0$ )? What kind of work has to be performed in order to create a design (create work diagram)? Starting with a tree diagram is useful to document all choices and alternatives.

### *Level 2: Definition of the input and output*

This level considers the input and output. Is there a need to feed pure reactants? How many products are produced? Is it necessary to include a purge? Is it necessary to include recycles (either or both gas/product/reactants)? Et cetera.

### *Level 3: Definition of the recycle structure*

Within this level the amount of reactor, separation and recycle systems is included. It is also decided whether feeding an excess of reactant to the process or a compressor is required.

### *Level 4: Definition of reaction and/or separation units*

The process units are selected and the interconnection is defined. Alternatives are created and extensively discussed within the next level.

### *Level 5: Evaluation of alternatives*

Here, it is important to list the alternatives and choices that are made. Listing the important design variables and estimating the optimum process conditions is useful to prove why a certain option is preferred above another at this level.

### *Level 6: Creating the process flow diagram*

The result from the discussion at level 5 is a process flow diagram (PFD). This diagram shows in detail which kind of unit operations are used and how these units are connected.

### *Level 7: Adding the heat-exchanger network*

Heat exchange is important for saving energy (costs) and is included in this level.

### *Level 8: Reviewing flexibility and adding control*

At this level, the flexibility of the designed system is discussed and the process control is included.

### *Level 9: Safety*

Finally, safety measures are discussed and included.

### Appendix D.3. Belbin analysis

Apart from discussing the planning and project organisation, it is also important to know which type of people are involved in the team. For this reason, a Belbin analysis is done. This is a kind of 'test' (on the website of Belbin, they state that it is not a test 'since there are no right or wrong answers' [113]) which results in the allocation of team roles to each member of the team. The allocation of these roles indicate the strong and weak points of the team. Nine team roles could be allocated [114]:

1. Plant: solves problems in unconventional ways, creative;
2. Monitor/Evaluator: focusses on facts, makes impartial judgements if necessary;
3. Co-ordinator: delegates work properly, focusses on the overall goal;
4. Resource investigators: connector between the world inside and outside a team;
5. Implementer: work efficient and are very practical;
6. Completer/Finisher: brings the almost final product to higher levels;
7. Team worker: are versatile and always work for the team;
8. Shaper: want that the team always keeps moving;
9. Specialist: someone with specific knowledge of a topic.

The main team roles of the team members are:

Stijn: Shaper, complete finisher

Michel: Implementer, monitor evaluator, specialist

Thimo: Monitor/evaluator, implementer

Anne: Implementer, complete finisher

Summarized:

- Shapers: 1
- Complete finishers: 2
- Implementers: 3
- Monitor/evaluator: 2
- Specialist: 1

The diagrams are shown on the next page.

The main conclusion that can be drawn from this summary, is that this project group is very action oriented. A lot of team roles overlap.

Three implementers in a team could cause issues, since all three are quite stubborn. This could be solved by Stijn, who (due to his shaper role) pushes to a solution. On the other hand, due to the presence of three implementers, the group is also very action oriented. So, this could solve an impasse and creates results quickly. The implementers could be too practical, which certainly has to be taken into account when something is not clear yet. The complete finishers point out that they focus on two different topics of finishing something: Stijn wants to have everything looking nice and Anne is more concerned about the structure.

Within the project group, 4 team roles are missing: Plant, team worker, resource investigator and coordinator. The most important thing is that a real coordinator is missing. Therefore, Thimo is asked

to try to be a coordinator (if necessary). On the other hand, there are several people within the project group who have experience with coordinating large activities.

Also a resource investigator is missing. However, based on the description of the resource investigator, Stijn thinks he is one as well.

The most important disadvantage of missing a plant, is the access to someone with a different point of view on the situation. This is solved by introducing brainstorm sessions within the brainstorm group, where the group tries to discuss different point of view on the topic.

To conclude, this action oriented group needs to make sure that they do not make decisions too quick and use the available time to come up with out of the box ideas.

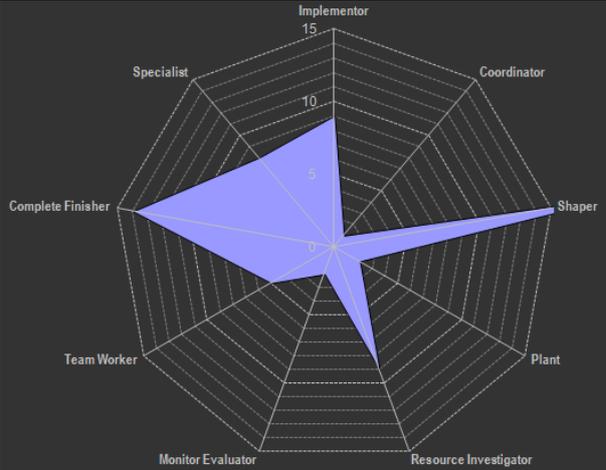


Figure 60: Stijn

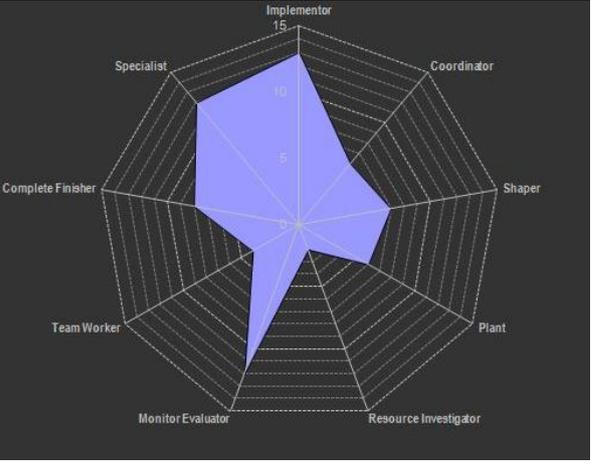


Figure 61: Michel

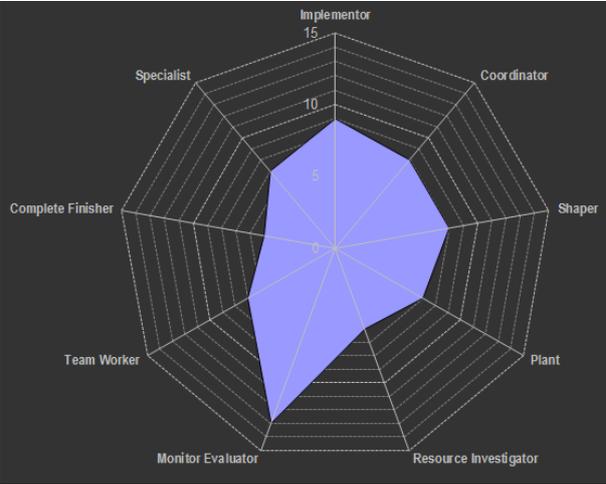


Figure 62: Thimo

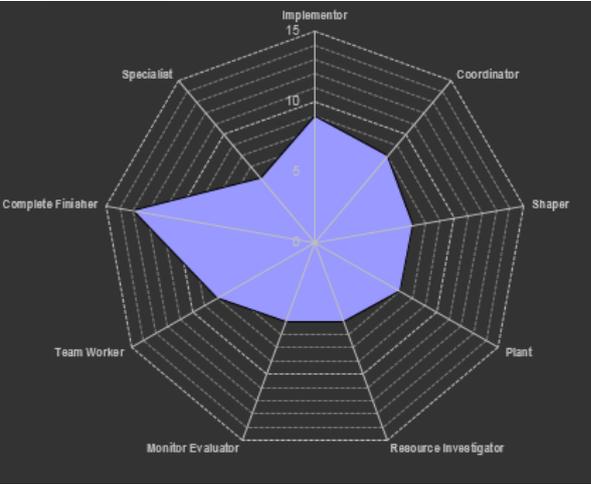


Figure 63: Anne

Appendix E Chapter 5 - Conceptual design

Appendix E.1. Block diagrams conceptual designs

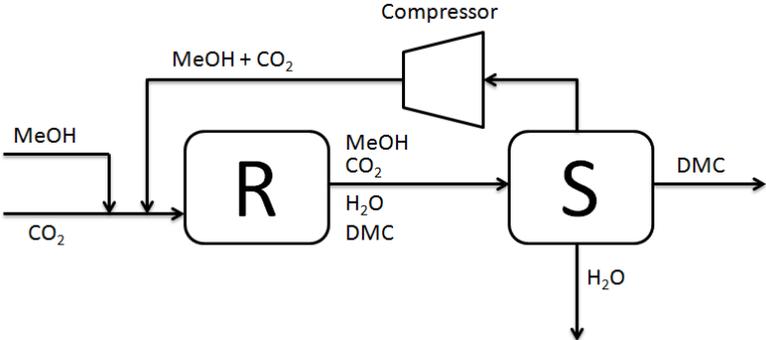


Figure 64: Block diagram of conceptual design 1.1

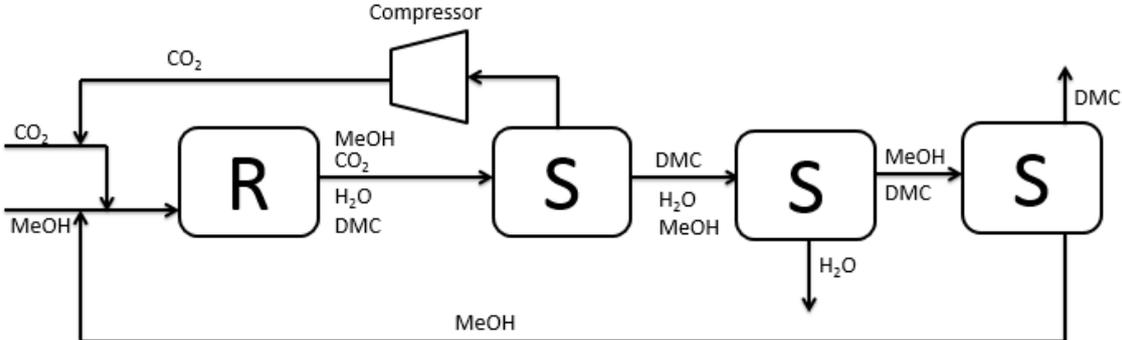


Figure 65: Block diagram of conceptual design 1.2

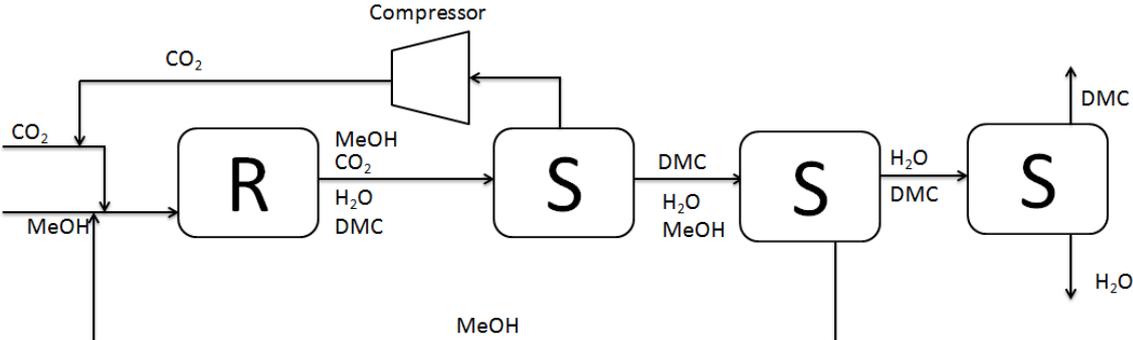


Figure 66: Block diagram of conceptual design 1.3

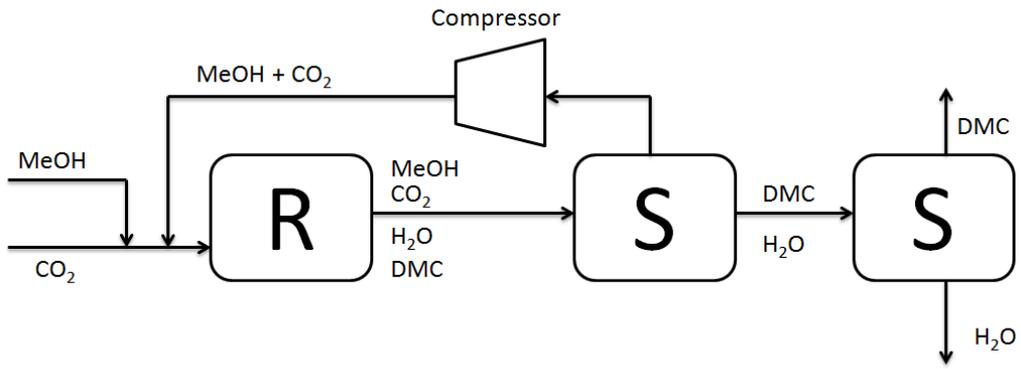


Figure 67: : Block diagram of conceptual design 1.4

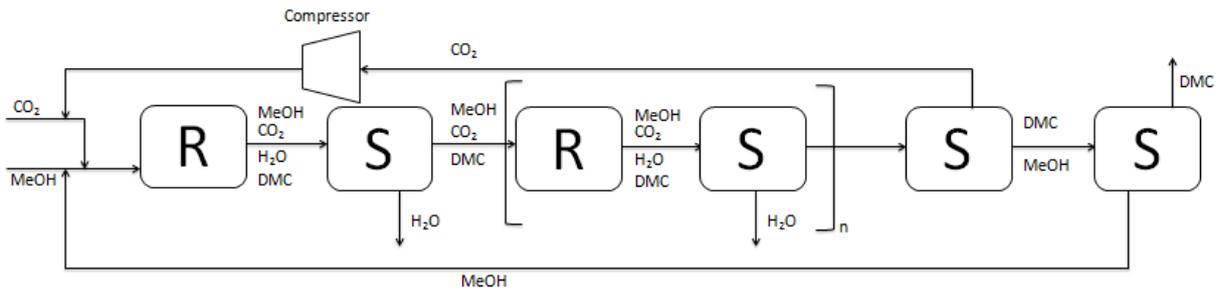


Figure 68: : Block diagram of conceptual design 1.5

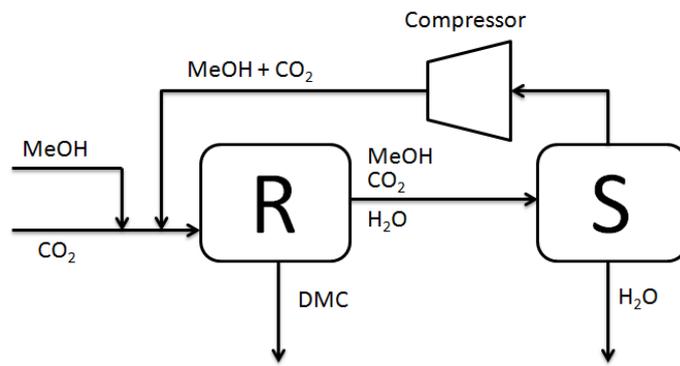


Figure 69: Block diagram of conceptual design 2.1

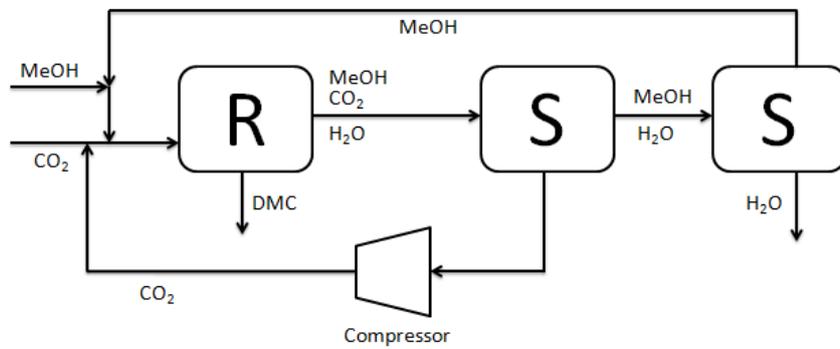


Figure 70: Block diagram of conceptual design 2.2

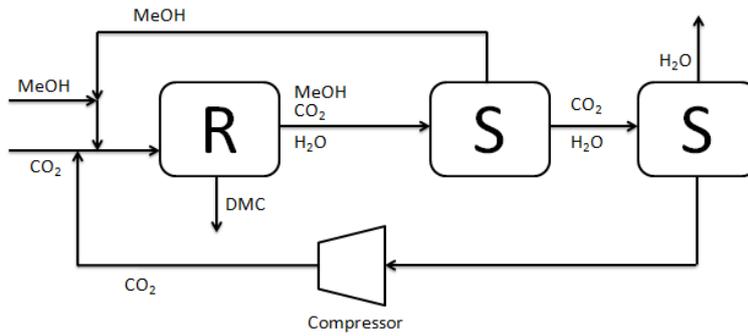


Figure 71: Block diagram of conceptual design 2.3

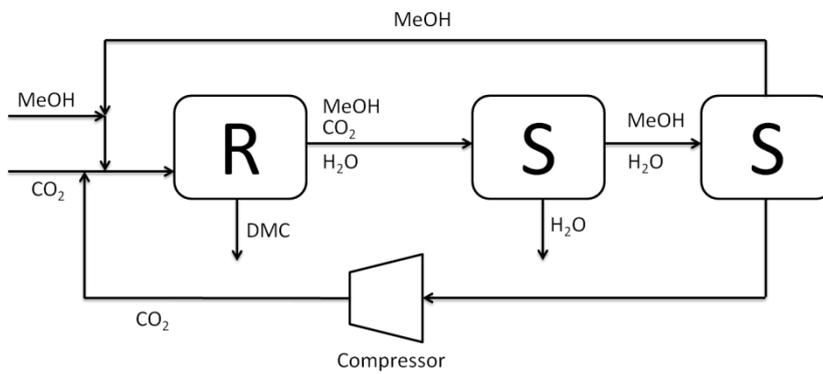


Figure 72: : Block diagram of conceptual design 2.4

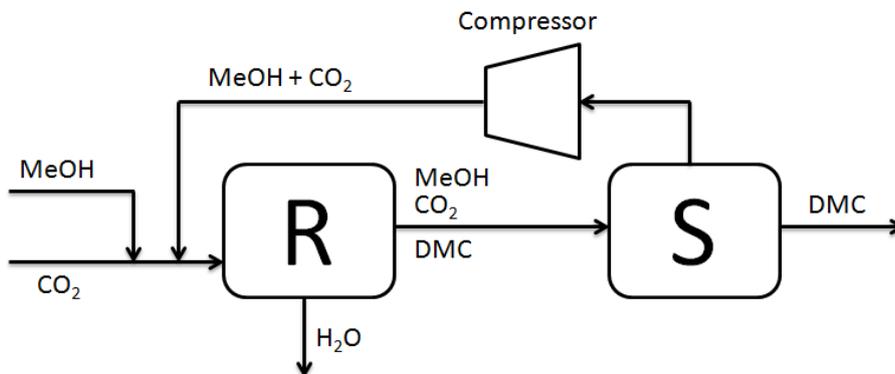


Figure 73: Block diagram of conceptual design 3.1

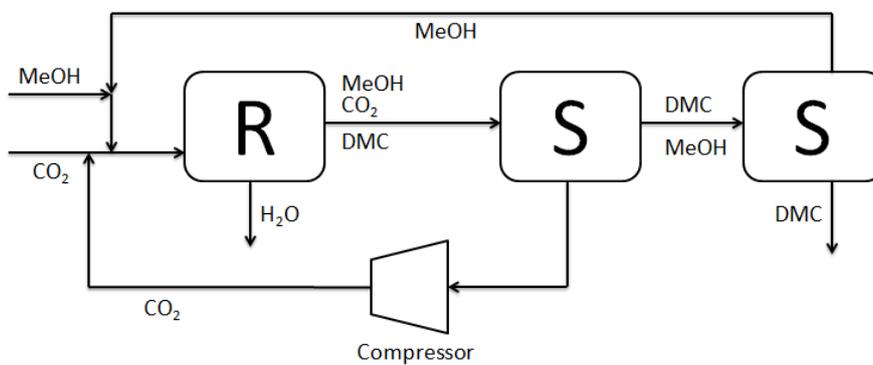


Figure 74: Block diagram of conceptual design 3.2

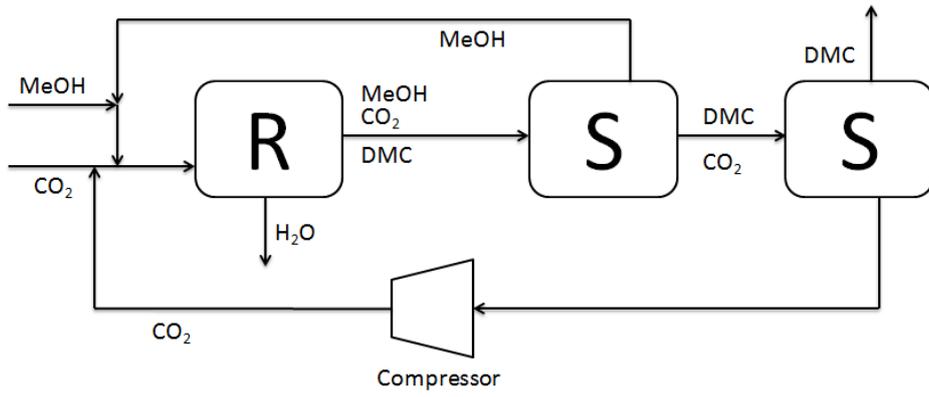


Figure 75: Block diagram of conceptual design 3.3

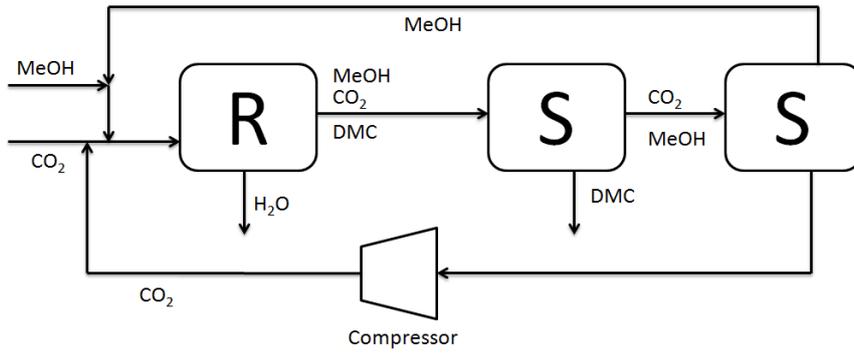


Figure 76: Block diagram of conceptual design 3.4

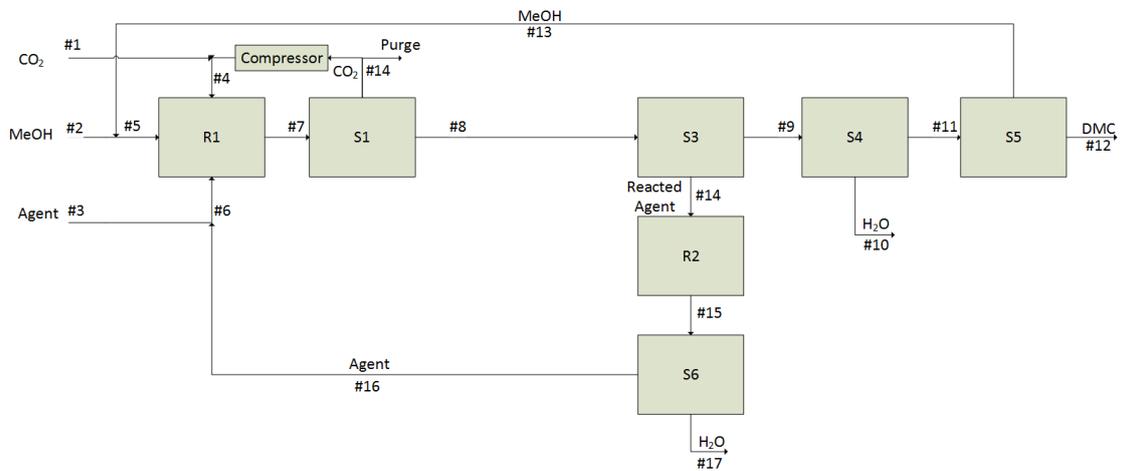


Figure 77: Conceptual design 4.1 with the incorporation of a dehydrating agent (without recycle for reactor 2)

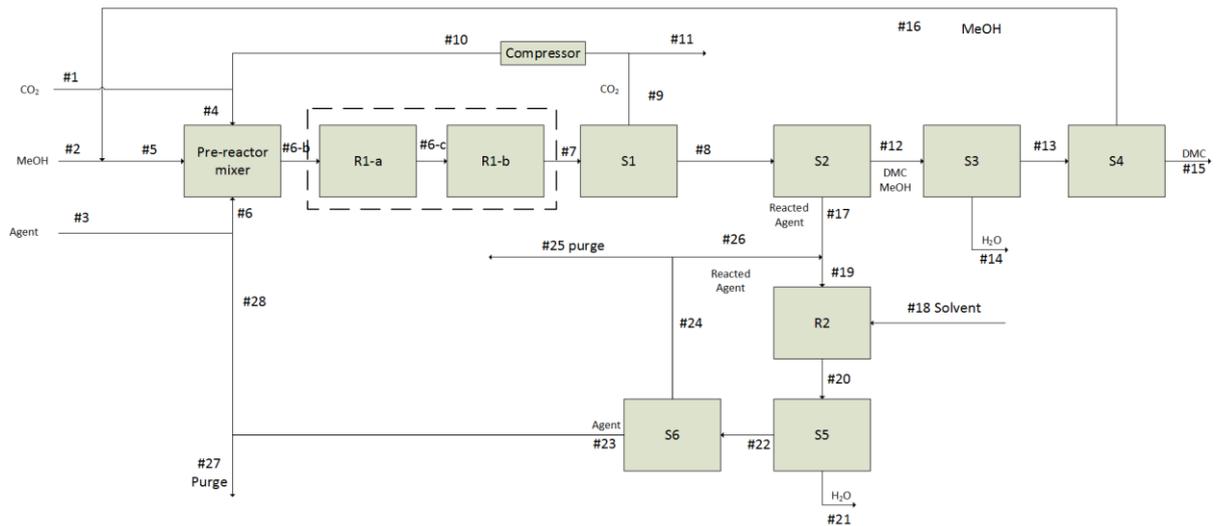


Figure 78: Conceptual design 4.2 with the incorporation of a dehydrating agent (including recycle for reactor 2). Pre-reactor mixing, R1-a and R1-b are actually just the first reactor, but splitting it in this way makes it more convenient for the global mass balance.

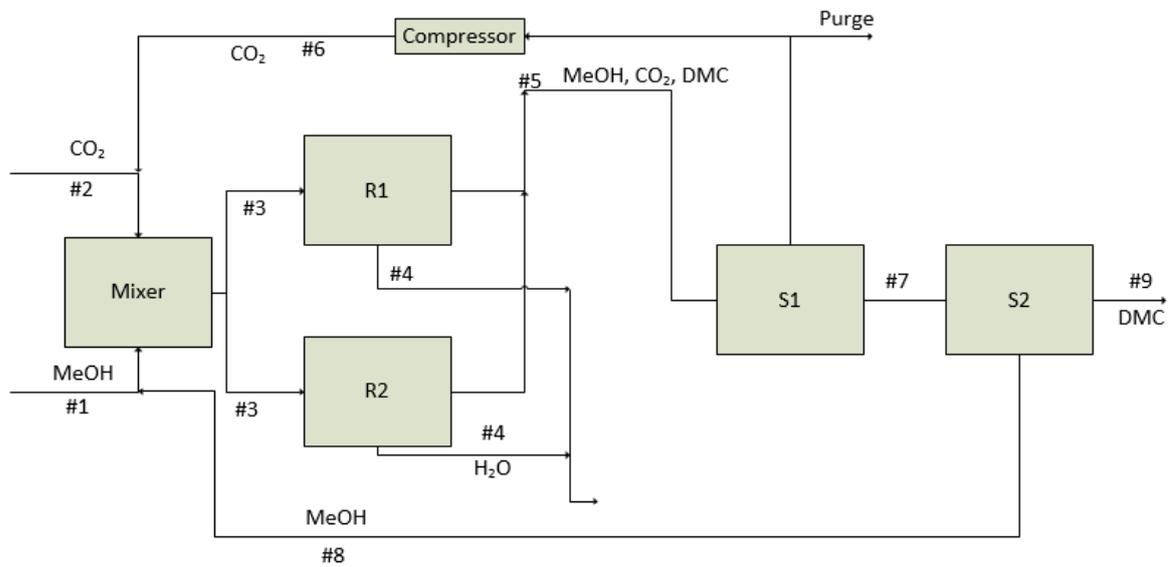


Figure 79: Conceptual design 4.3 with a dehydrating agent in a semi-continuous reactor system

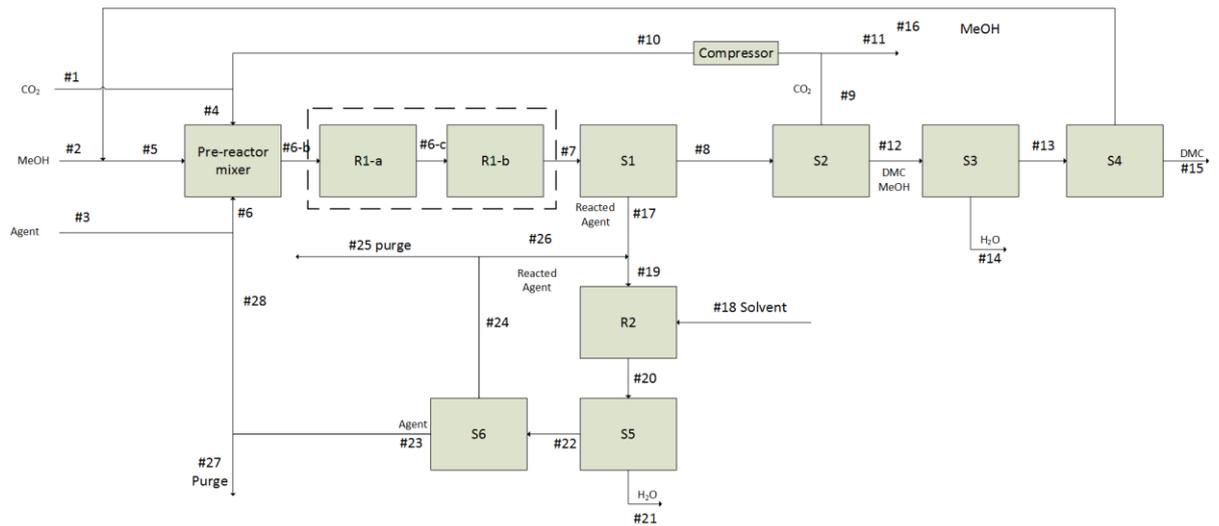


Figure 80: Conceptual design 4.4 with first the separation of the dehydrating agent. R1 is split into a pre-mixer, R1-a and R1-b to make is more convenient for the global mass balance.

Appendix E.2. Global mass balance

mol/s	#1	#2	#3	#4	#5	#6	#6-b	#6-c	#7	#8	#9	#10	#11	#12	#13
CO2	190.000	0.000	0.000	933.455	0.000	0.000	933.455	758.628	758.628	0.000	758.628	743.455	15.173	0.000	0.000
MeOH	0.000	350.000	0.000	5.637	372.778	0.000	378.414	28.759	28.759	23.008	5.752	5.637	0.115	23.008	23.008
DMC	0.000	0.000	0.000	9.099	1.764	0.000	10.863	185.690	185.690	176.406	9.285	9.099	0.186	176.406	176.406
H2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	174.827	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-cyanopyridine	0.000	0.000	15.800	0.000	0.000	188.984	188.984	188.984	14.157	14.157	0.000	0.000	0.000	0.000	0.000
2-picolinamide	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	174.827	174.827	0.000	0.000	0.000	0.000	0.000
<b>Totaal</b>	<b>190.000</b>	<b>350.000</b>	<b>15.800</b>	<b>948.191</b>	<b>374.542</b>	<b>188.984</b>	<b>1511.717</b>	<b>1336.890</b>	<b>1162.062</b>	<b>388.398</b>	<b>773.664</b>	<b>758.191</b>	<b>15.473</b>	<b>199.413</b>	<b>199.413</b>

mol/s	#14	#15	#16	#17	#18	#19	#20	#21	#22	#23	#24	#25	#26	#27	#28
CO2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00	0.00
MeOH	0.000	0.230	22.778	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00	0.00
DMC	0.000	174.642	1.764	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00	0.00
H2O	0.000	0.000	0.000	0.000	0.000	0.000	171.863	171.863	0.000	0.000	0.00	0.00	0.00	0.00	0.00
2-cyanopyridine	0.000	0.000	0.000	14.157	0.000	14.157	186.020	9.301	176.719	176.719	0.00	0.00	0.00	3.53	173.18
2-picolinamide	0.000	0.000	0.000	174.827	0.000	214.829	42.966	2.148	40.817	0.000	40.82	0.82	40.00	0.00	0.00
<b>Totaal</b>	<b>0.000</b>	<b>174.872</b>	<b>24.542</b>	<b>188.984</b>	<b>0.000</b>	<b>228.986</b>	<b>400.848</b>	<b>183.312</b>	<b>217.536</b>	<b>176.719</b>	<b>40.817</b>	<b>0.816</b>	<b>40.001</b>	<b>3.534</b>	<b>173.184</b>

Figure 81: A global mole balance of conceptual design 4.2

kg/s	#1	#2	#3	#4	#5	#6	#6-b	#6-c	#7	#8	#9	#10	#11	#12	#13
CO2	8.362	0.000	0.000	41.080	0.000	0.000	41.080	33.386	33.386	0.000	33.386	32.718	0.668	0.000	0.000
MeOH	0.000	11.214	0.000	0.181	11.944	0.000	12.125	0.921	0.921	0.737	0.184	0.181	0.004	0.737	0.737
DMC	0.000	0.000	0.000	0.820	0.159	0.000	0.978	16.726	16.726	15.890	0.836	0.820	0.017	15.890	15.890
H2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	3.150	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-cyanopyridine	0.000	0.000	1.645	0.000	0.000	19.674	19.674	19.674	1.474	1.474	0.000	0.000	0.000	0.000	0.000
2-picolinamide	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	21.350	21.350	0.000	0.000	0.000	0.000	0.000
<i>Totaal</i>	<i>8.362</i>	<i>11.214</i>	<i>1.645</i>	<i>42.080</i>	<i>12.103</i>	<i>19.674</i>	<i>73.857</i>	<i>73.857</i>	<i>73.857</i>	<i>39.451</i>	<i>34.406</i>	<i>33.718</i>	<i>0.688</i>	<i>16.627</i>	<i>16.627</i>
kg/s	#14	#15	#16	#17	#18	#19	#20	#21	#22	#23	#24	#25	#26	#27	#28
CO2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
MeOH	0.000	0.007	0.730	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
DMC	0.000	15.731	0.159	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H2O	0.000	0.000	0.000	0.000	0.000	0.000	3.096	3.096	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-cyanopyridine	0.000	0.000	0.000	1.474	0.000	1.474	19.366	0.968	18.397	18.397	0.000	0.000	0.000	0.368	18.030
2-picolinamide	0.000	0.000	0.000	21.350	0.000	26.235	5.247	0.262	4.985	0.000	4.985	0.100	4.885	0.000	0.000
<i>Totaal</i>	<i>0.000</i>	<i>15.738</i>	<i>0.889</i>	<i>22.824</i>	<i>0.000</i>	<i>27.709</i>	<i>27.709</i>	<i>4.327</i>	<i>23.382</i>	<i>18.397</i>	<i>4.985</i>	<i>0.100</i>	<i>4.885</i>	<i>0.368</i>	<i>18.030</i>

Figure 82: Global mass balance of conceptual design 4.2

## Appendix F Chapter 6 - Index flowsheet

### Appendix F.1. UNISIM

#### F.1.1. UNISIM fluid package

The software package UNISIM is used to simulate the process. To create a reliable simulation, the choice for a fluid package is crucial. The following aspects are important for the selection of a thermodynamic model namely: chemical species, pressure and temperature ranges, phases involved and the availability of data [115].

Due to the formation of an azeotrope between DMC and methanol only activity coefficient models such as NRTL, UNIQUAC and UNIFAC are suitable. Wherefrom NRTL is chosen as the model to use. Mainly because of availability of the data and validity of the data (Check F.1.3 for validity of the models).

Redlich Kwong is chosen as the model used for the vapour phase. It should be suitable at the chosen operating conditions.

#### F.1.2. Boundary conditions

For the UNISIM simulation some boundary conditions must be set or determined

- Cooling can be done down to 20°C with cooling water. This assumption is not entirely valid, because cooling water is usually available at 20°C, though there should be accounted for a  $\Delta T$  of at least 10°C for heaters/coolers/heat exchangers.
- The maximum output temperature of a compressor was set at 150°C. Maximum  $\Delta T$  of 100°C. Interstage compression was used in case one of these criteria are exceeded.
- For distillation columns minimum reflux was determined in case solver gave stable solutions. This was done by using a column as big as possible (preferably 200 trays, feed tray may differ). Then set the most important spec and see what the reflux is, or if the reflux is the second spec, then minimizing the reflux as long the simulator gives a solution.
- DMC, 2-cyanopyridine and 2-picolinamide are not available in the database of UNISIM. Therefore, these are added as hypothetical compounds. Data for the compounds is imported from ASPEN (for DMC) and/or literature.
- Reboiler duty of columns is indicator for energy usage. Condenser can simply be cooled by cooling water, energy for pumping can be neglected.

#### F.1.3. DMC/Methanol separation

Data about DMC is not available in UNISIM. Therefore data for DMC is mainly imported from ASPEN plus. To construct a VLE diagram, interaction parameters between the compounds must be known. Parameters for different models were obtained from the software package ASPEN and the DECHEMA data series. The VLE graph was constructed by the software package UNISIM by the mentioned parameters. These were compared with experimental data from Rodriguez et al. [61]. It followed that a NRTL model with parameters from ASPEN do fit the literature data best. The graphs are shown in Figure 83.

#### F.1.4. Solvent Interaction

Phenol was used in the first place as an entrainer for extractive distillation. To be able to successfully simulate this type of distillation interaction parameters between the compounds need to be known. Interaction parameters for DMC with phenol and methanol with phenol were obtained from Hu et al. [69]. VLE diagrams were constructed in UNISIM based on these interaction parameters. Thereafter, these diagrams were compared with the original literature data of Hu et al., to make sure that the UNISIM simulation is based on correct VLE data. Results are displayed in Figure 84 and Figure 85, they show a perfect fit. Therefore, the mentioned VLE diagrams are valid to work with in UNISIM. The same was done for 2-ethoxyethanol and 4-methyl-2-pentanone [70]. Their T-xy diagrams with DMC deviate slightly. This was also the case at 99.32kPa, wherefore data was also available. However, the deviation is small and about as big at both pressures. Therefore, it is assumed that simulation is reliable enough.

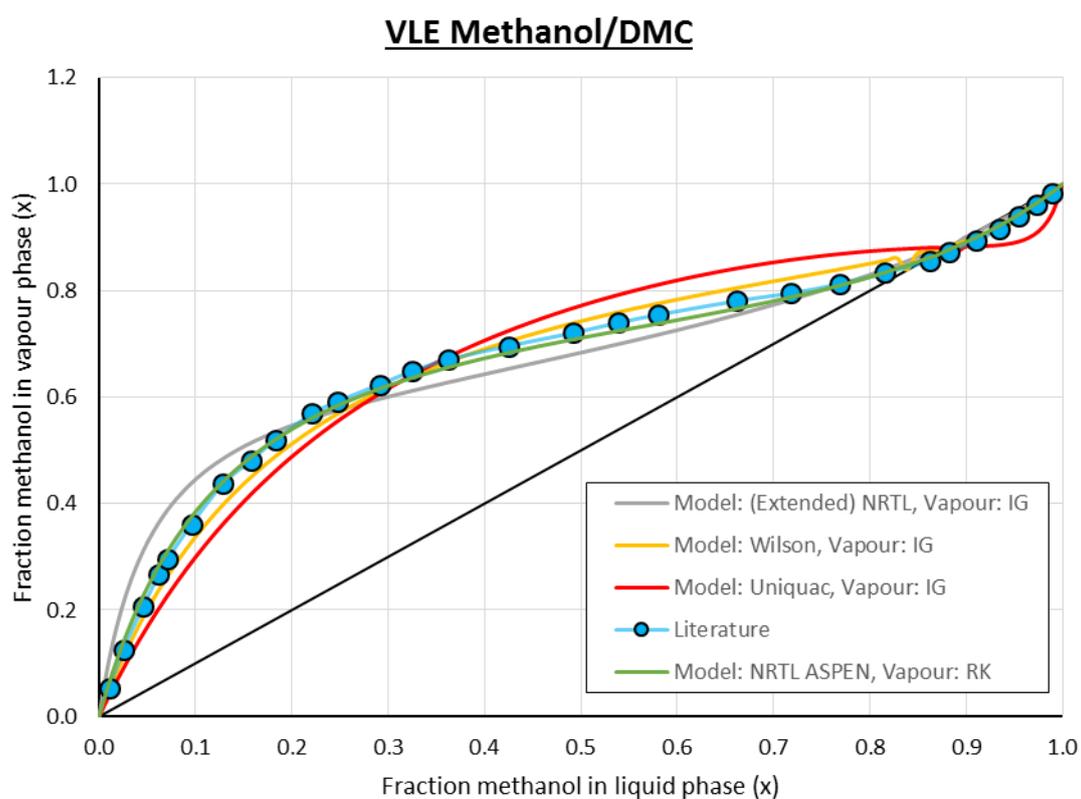


Figure 83: Model comparison with literature data, results obtained from UNISIM, parameters obtained from DECHEMA data series and ASPEN Plus software package, experimental data from Rodriguez et al.

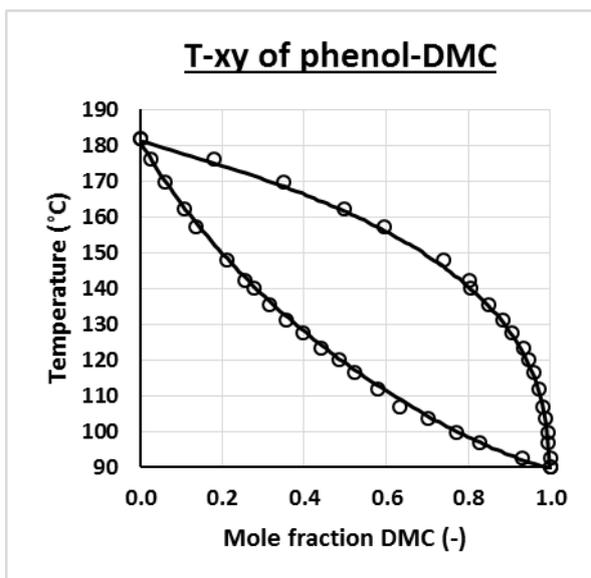


Figure 84: T-xy of phenol-DMC, based on NRTL parameters of HU et al. [69]

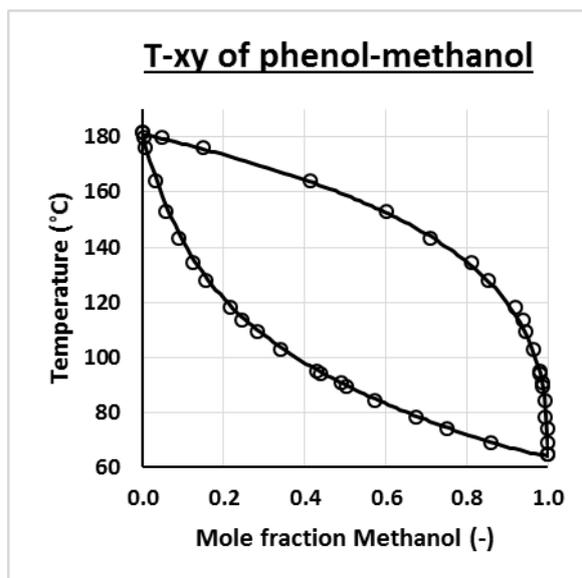


Figure 85: T-xy of phenol-Methanol, based on NRTL parameters of HU et al. [69]

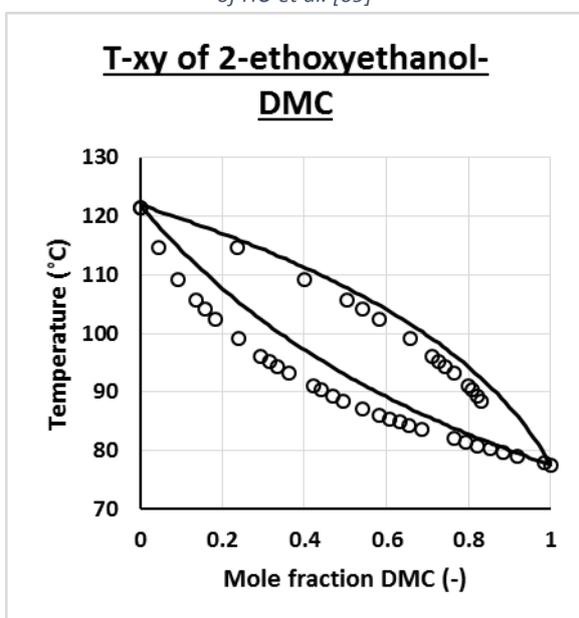


Figure 86: T-xy of 2-ethoxyethanol-DMC at 66kPa, based on NRTL parameters of Matsuda et al. [70]

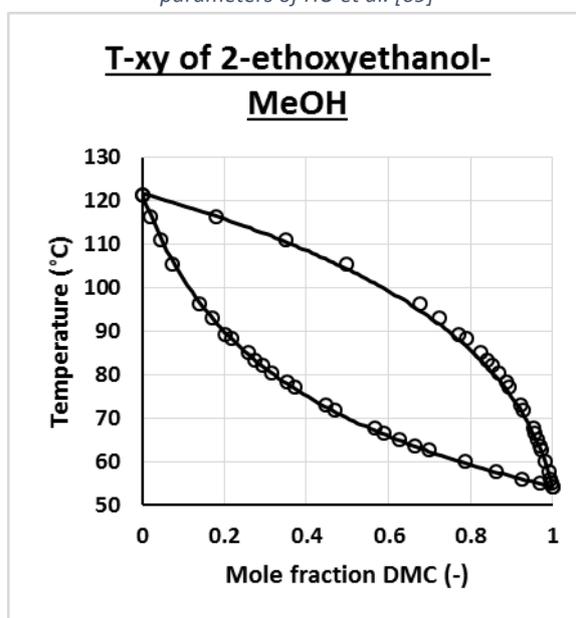


Figure 87: T-xy of 2-ethoxyethanol-MeOH at 66kPa, based on NRTL parameters of Matsuda et al. [70]

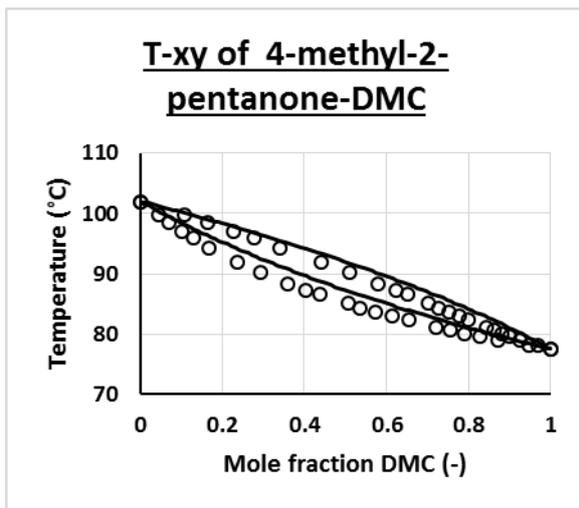


Figure 88: T-xy of 4-methyl-2-pentanone-DMC at 66kPa, based on NRTL parameters of Matsuda et al. [70]

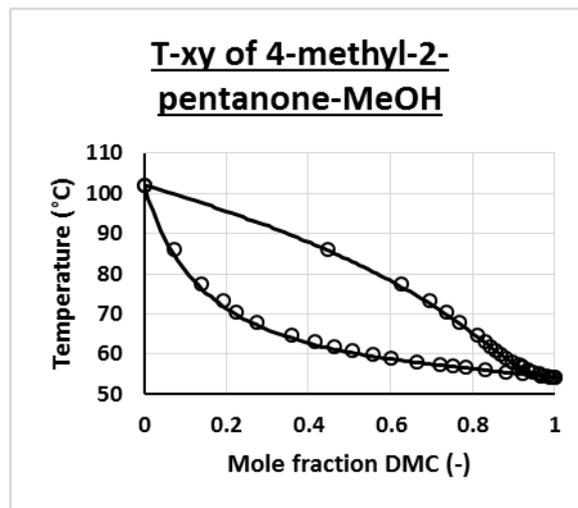
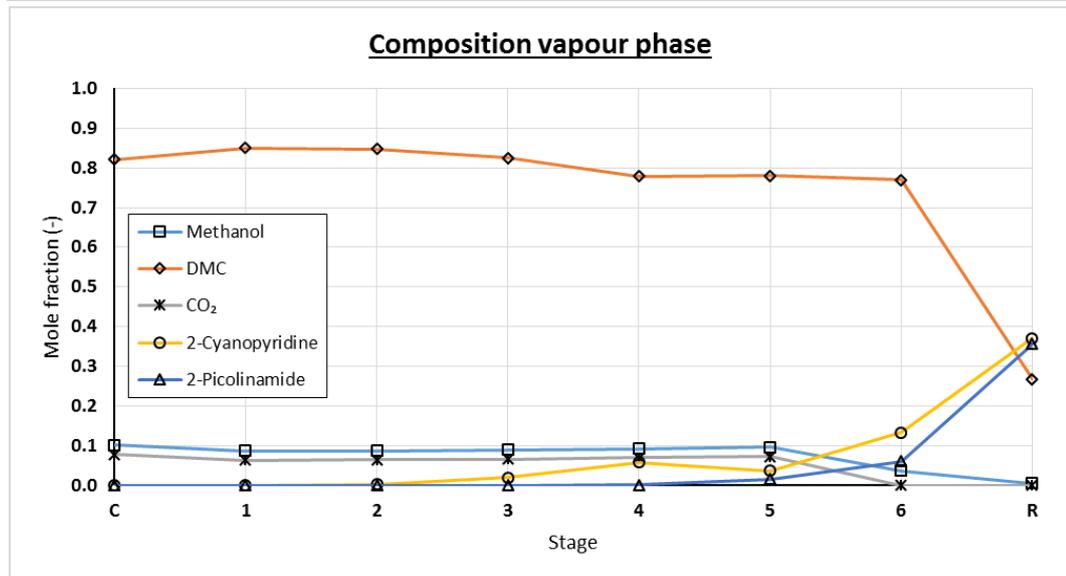
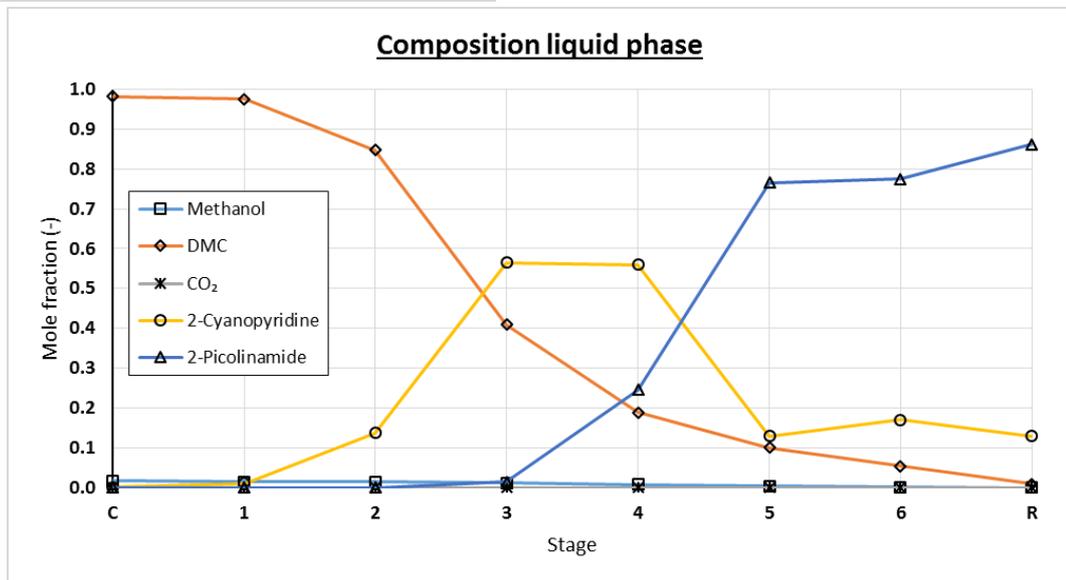
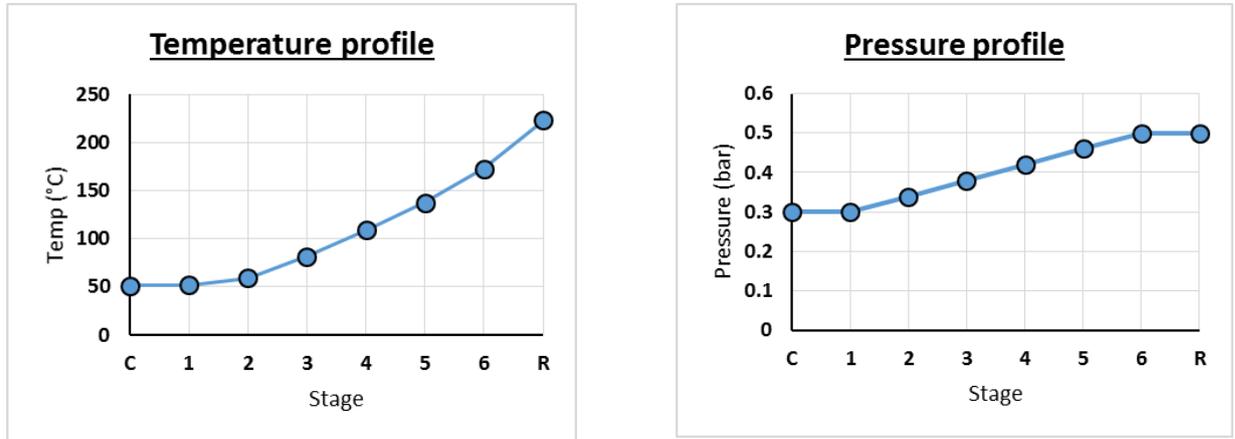


Figure 89: T-xy of 4-methyl-2-pentanone-MeOH at 66kPa, based on NRTL parameters of Matsuda et al. [70]

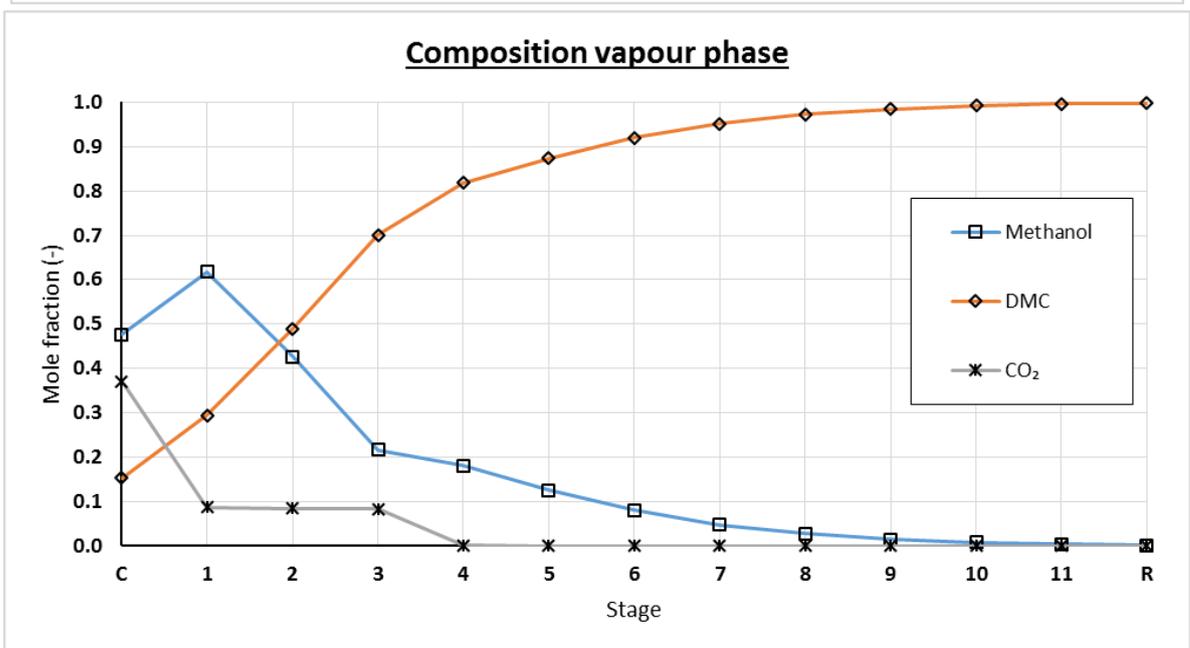
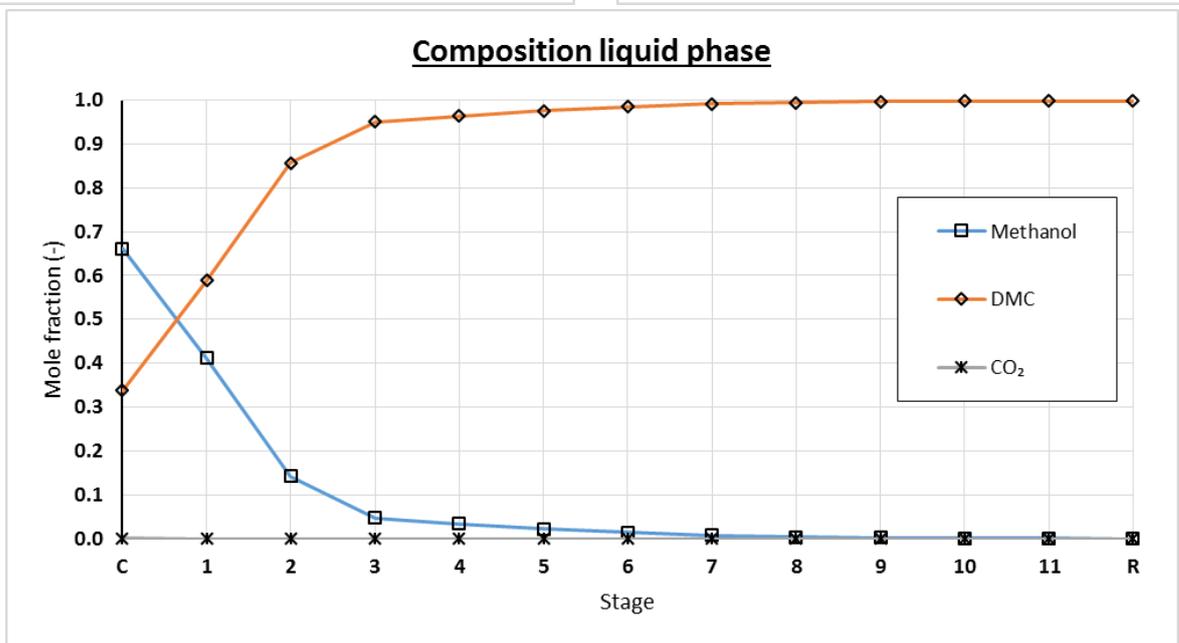
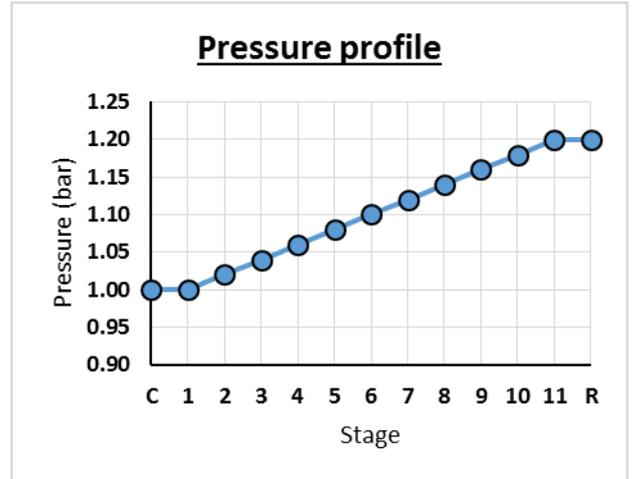
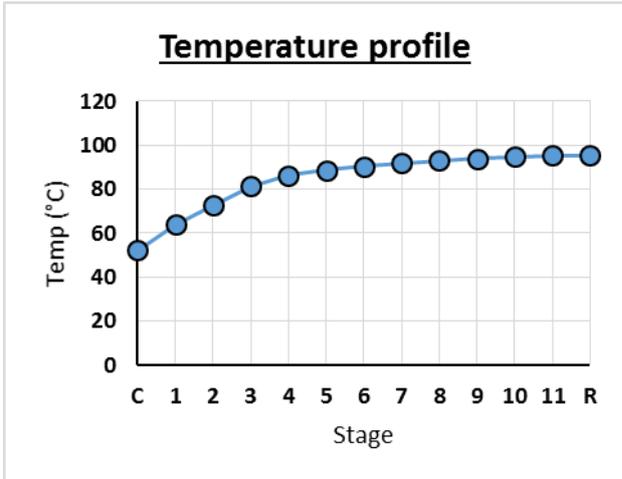
### F.1.5. Column profiles from UNISIM simulation

The composition, temperature and pressure profile of all distillation columns are shown below in this paragraph. The trays are excluding reboiler and condenser.

**Description: T-2071, 6 Trays, Reflux: 0.216, Feed tray: 5, Solvent Feed tray: -**

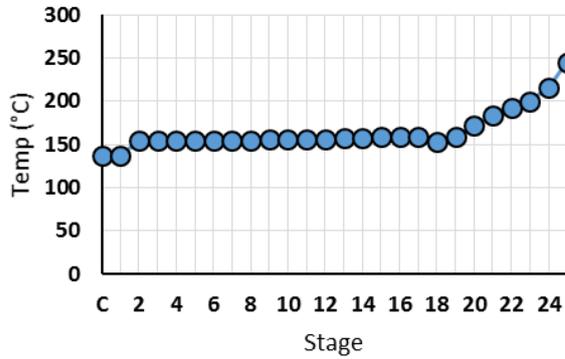


Description: T-2072, 11 Trays, Reflux: 3.28, Feed tray: 3, Solvent Feed tray: -

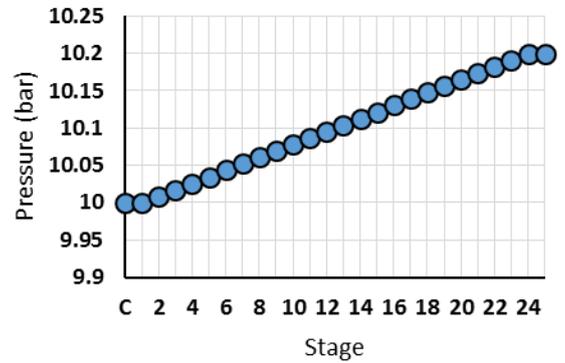


Description: T-2073, 24 Trays, Reflux: 1.8, Feed tray: 18, Solvent Feed tray: 2

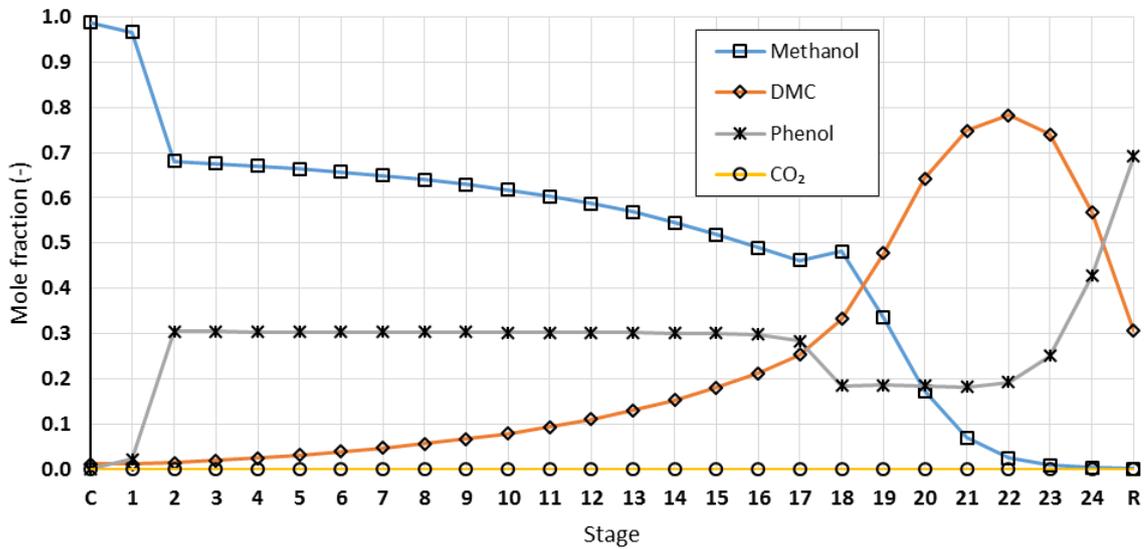
**Temperature profile**



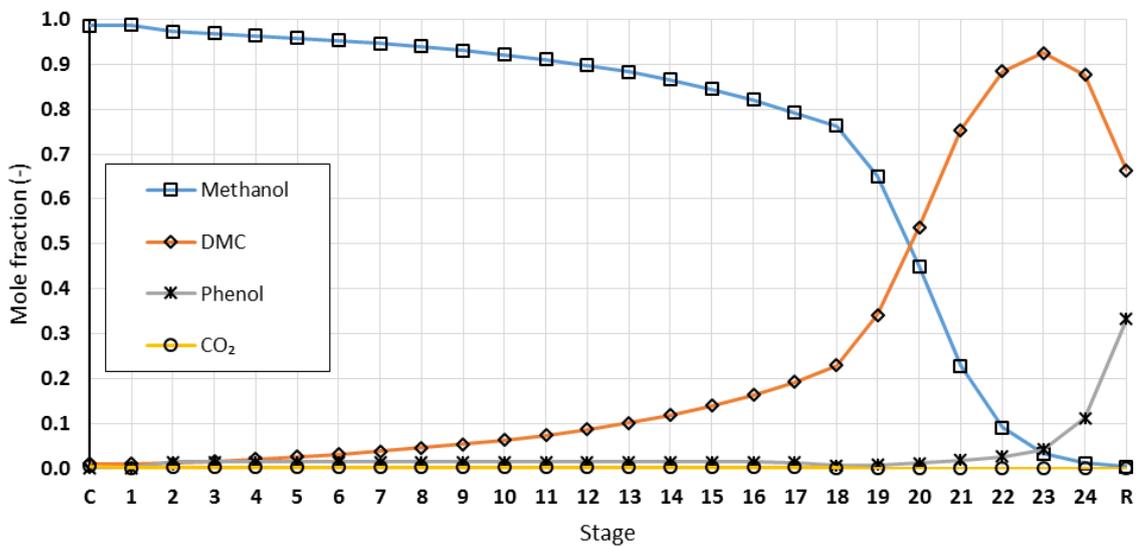
**Pressure profile**



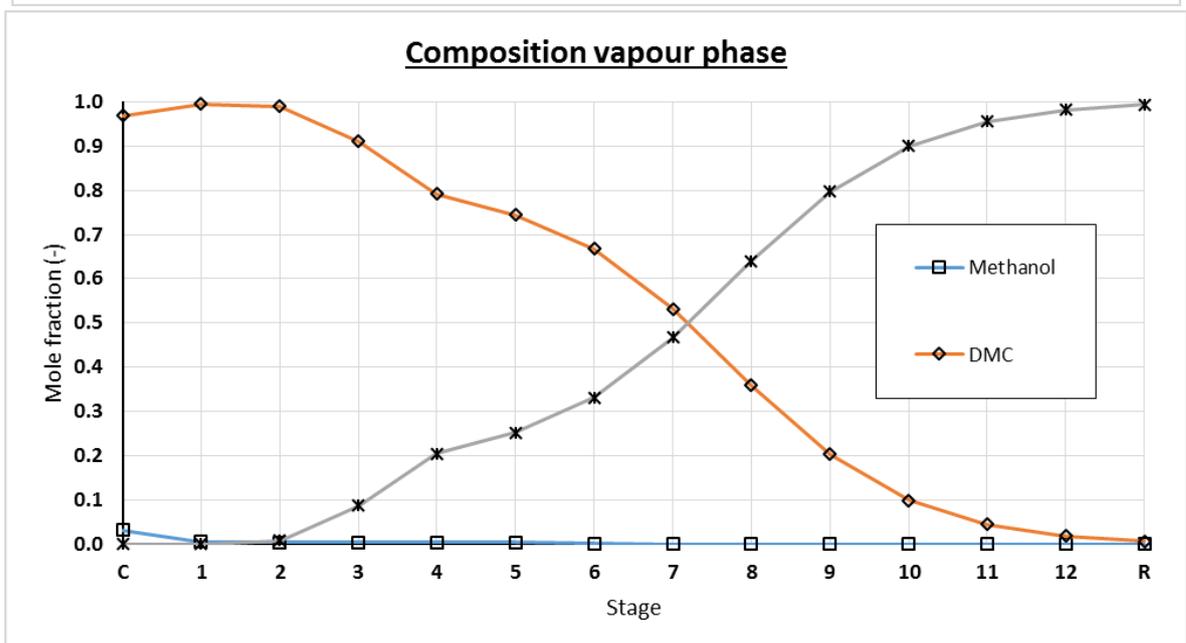
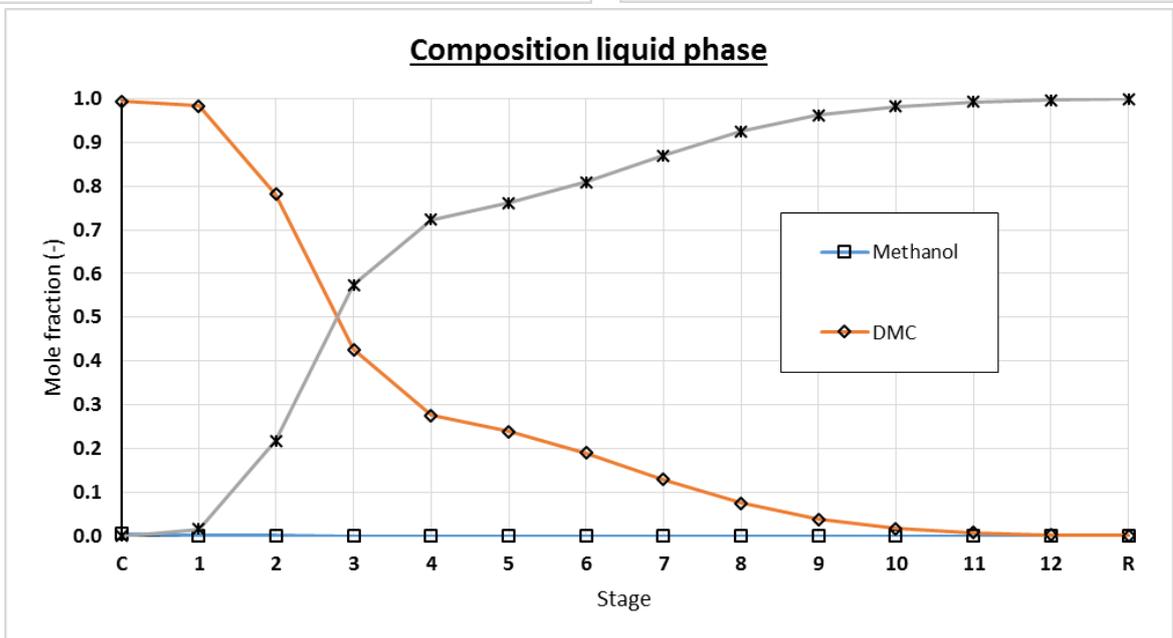
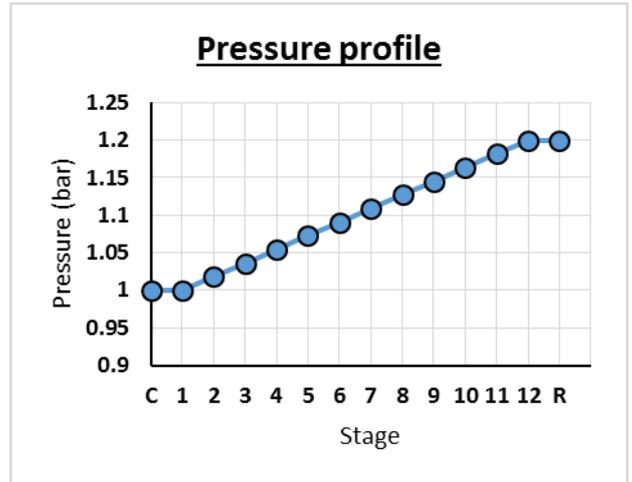
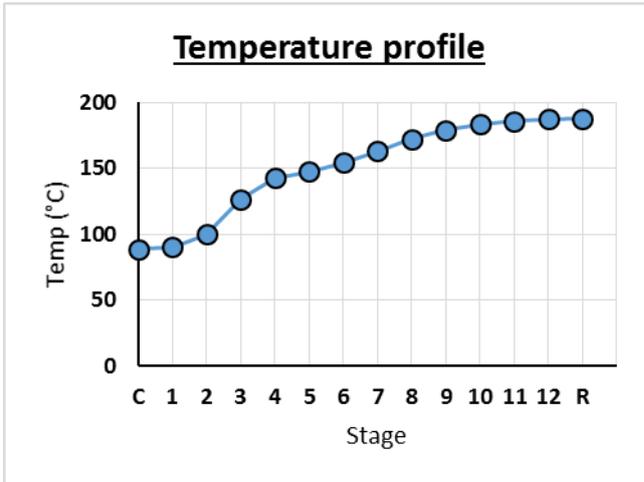
**Composition liquid phase**



**Composition vapour phase**



Description: T-2074, 12 Trays, Reflux: 0.83, Feed tray: 5, Solvent Feed tray: -



Appendix F.2. Decision tree unit operations

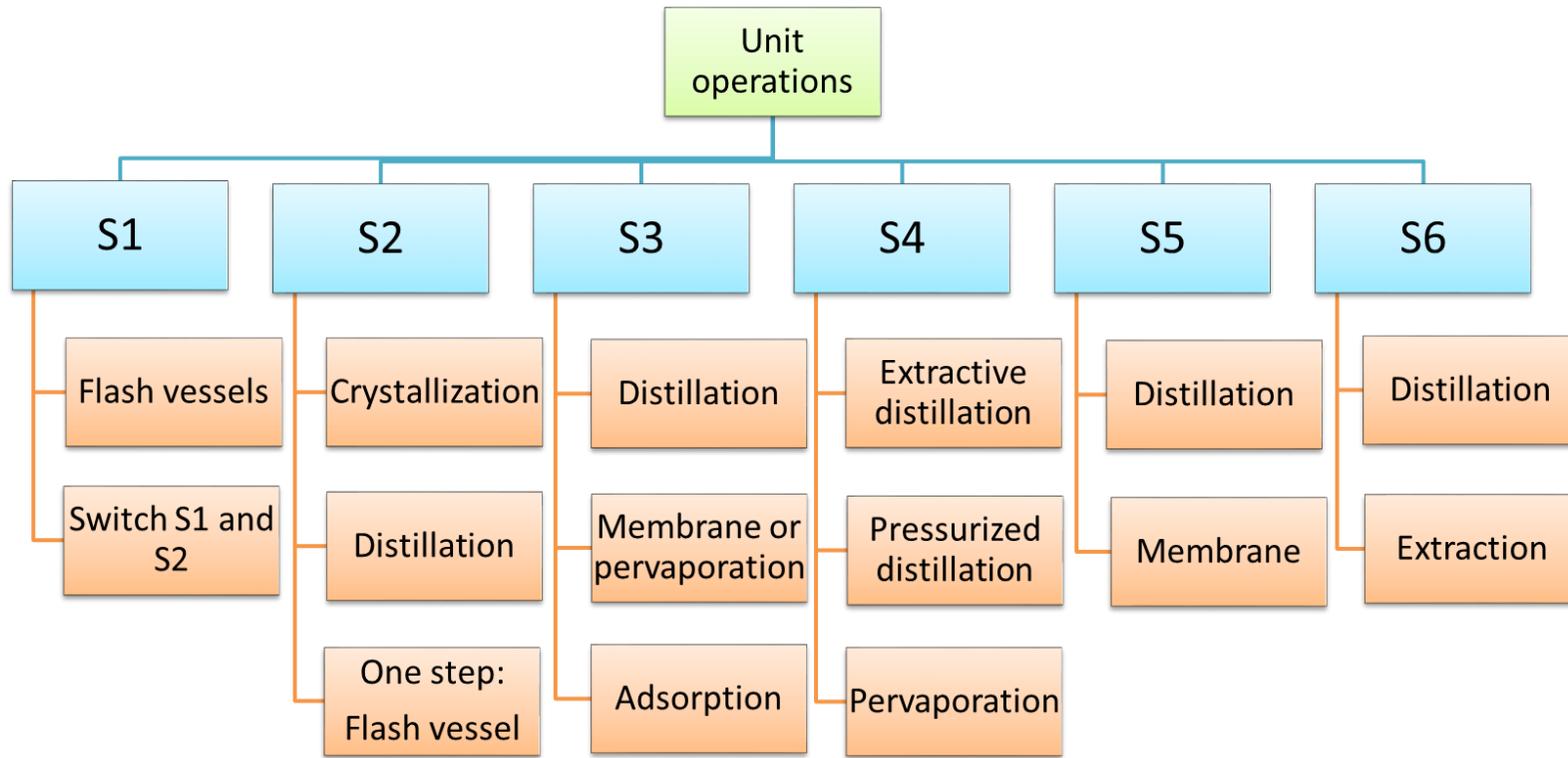


Figure 90: Decision tree unit operations

Appendix F.3. Decision tree separations

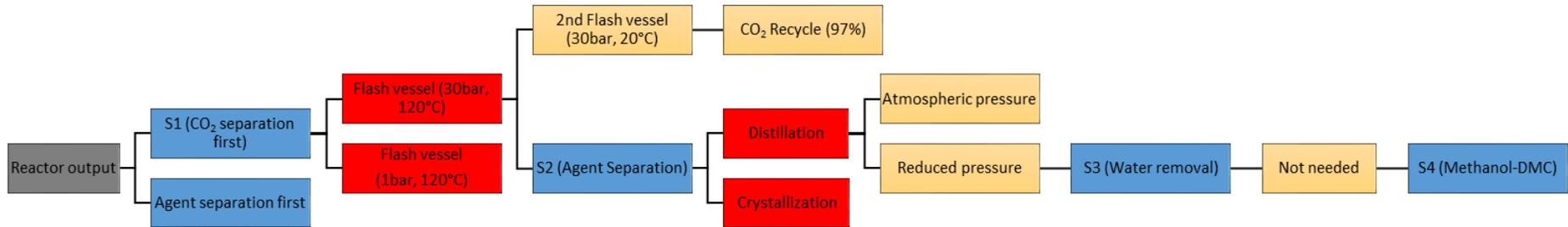


Figure 91: Decision tree separations, excluding S4

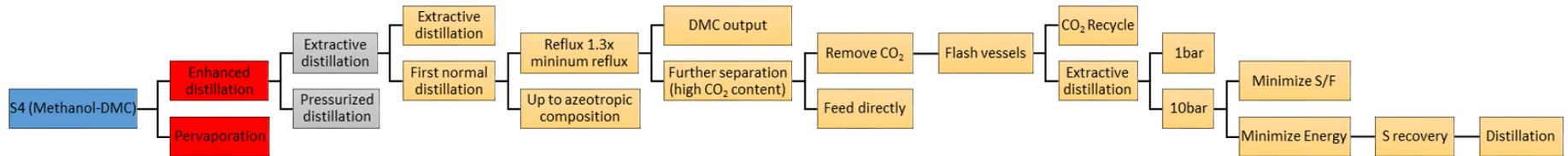


Figure 92: Decision tree separation, S4

Appendix F.4. Index flow sheet

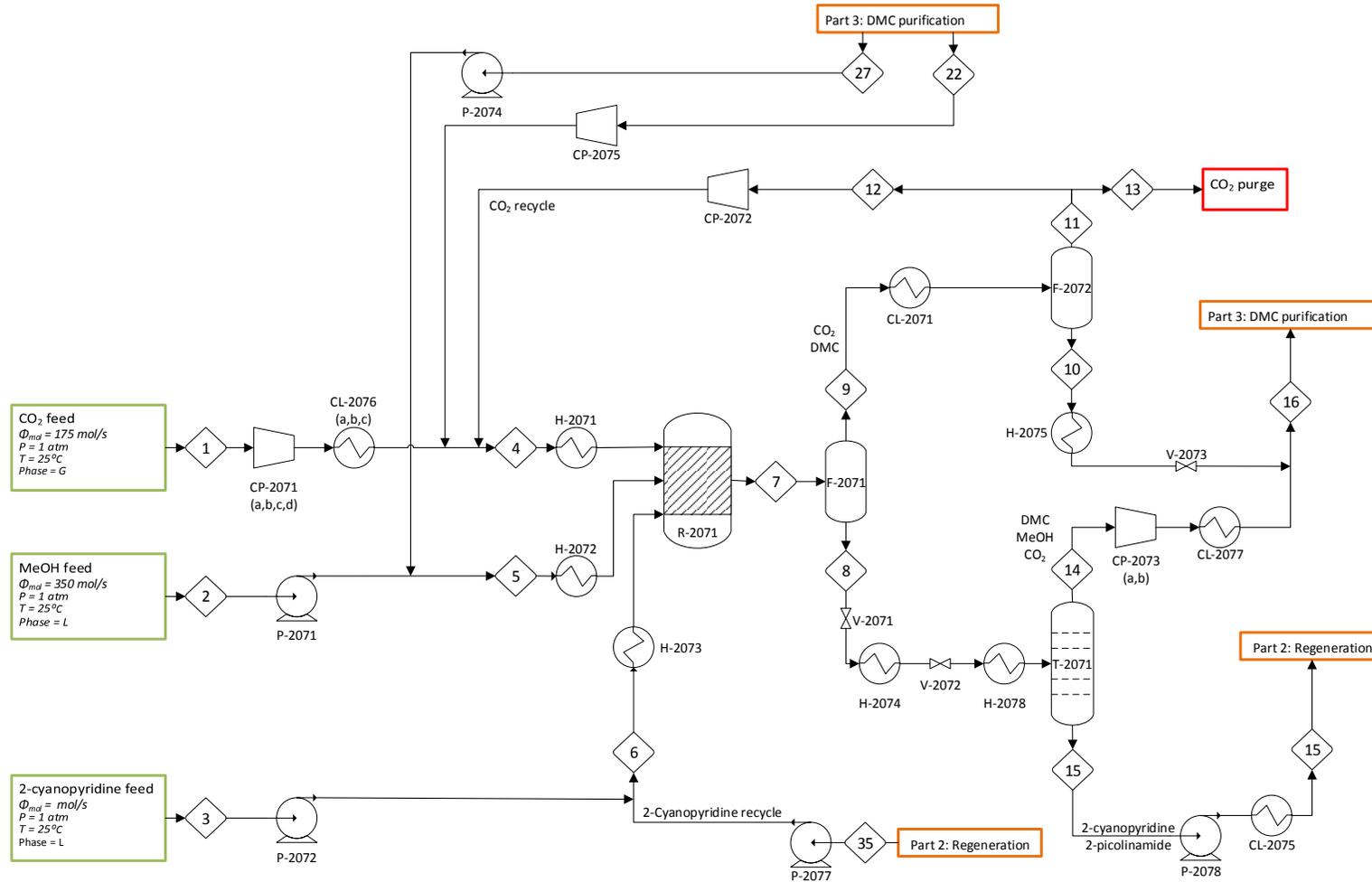


Figure 93: Index flowsheet - part one

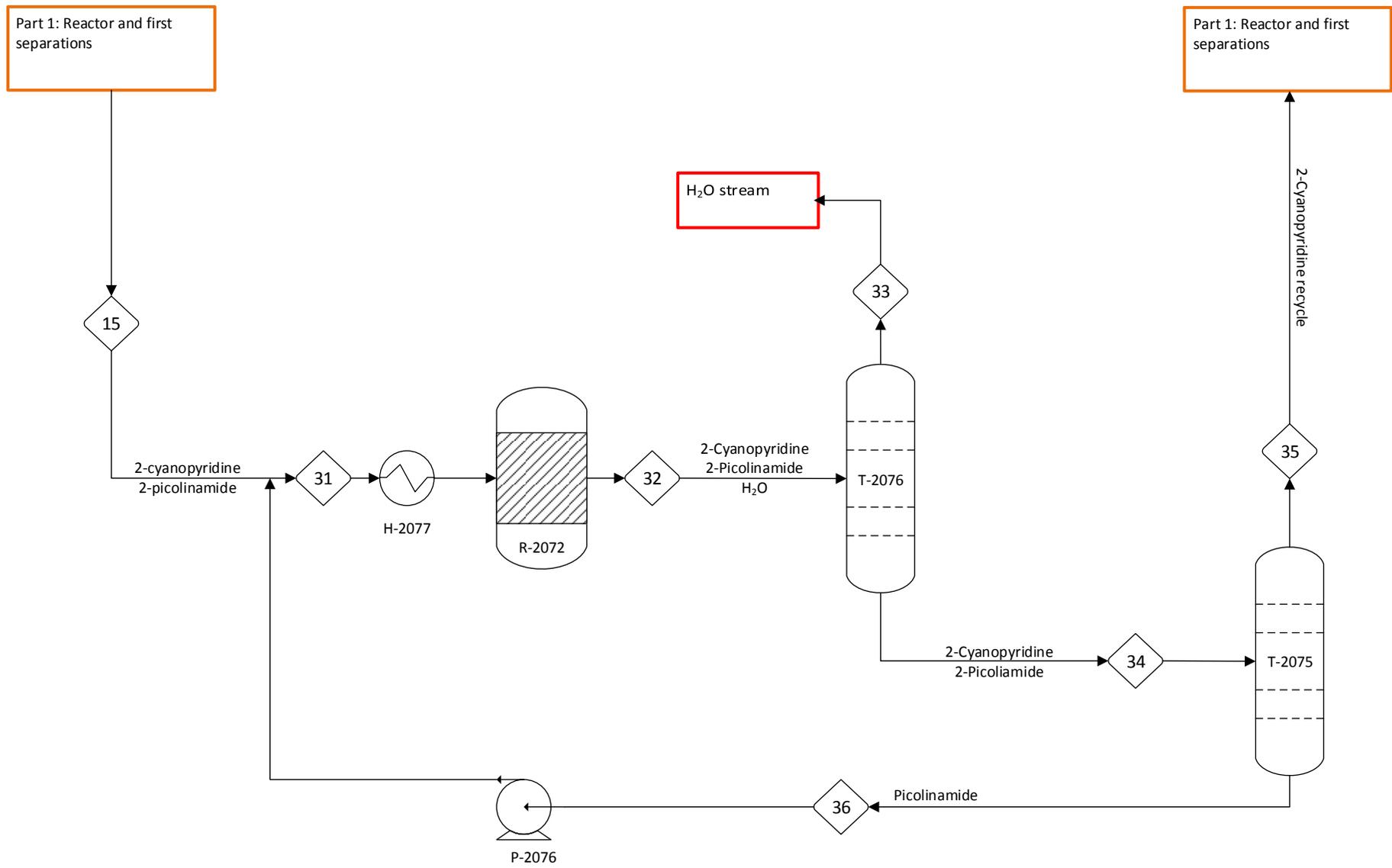


Figure 94: Index flowsheet - part two

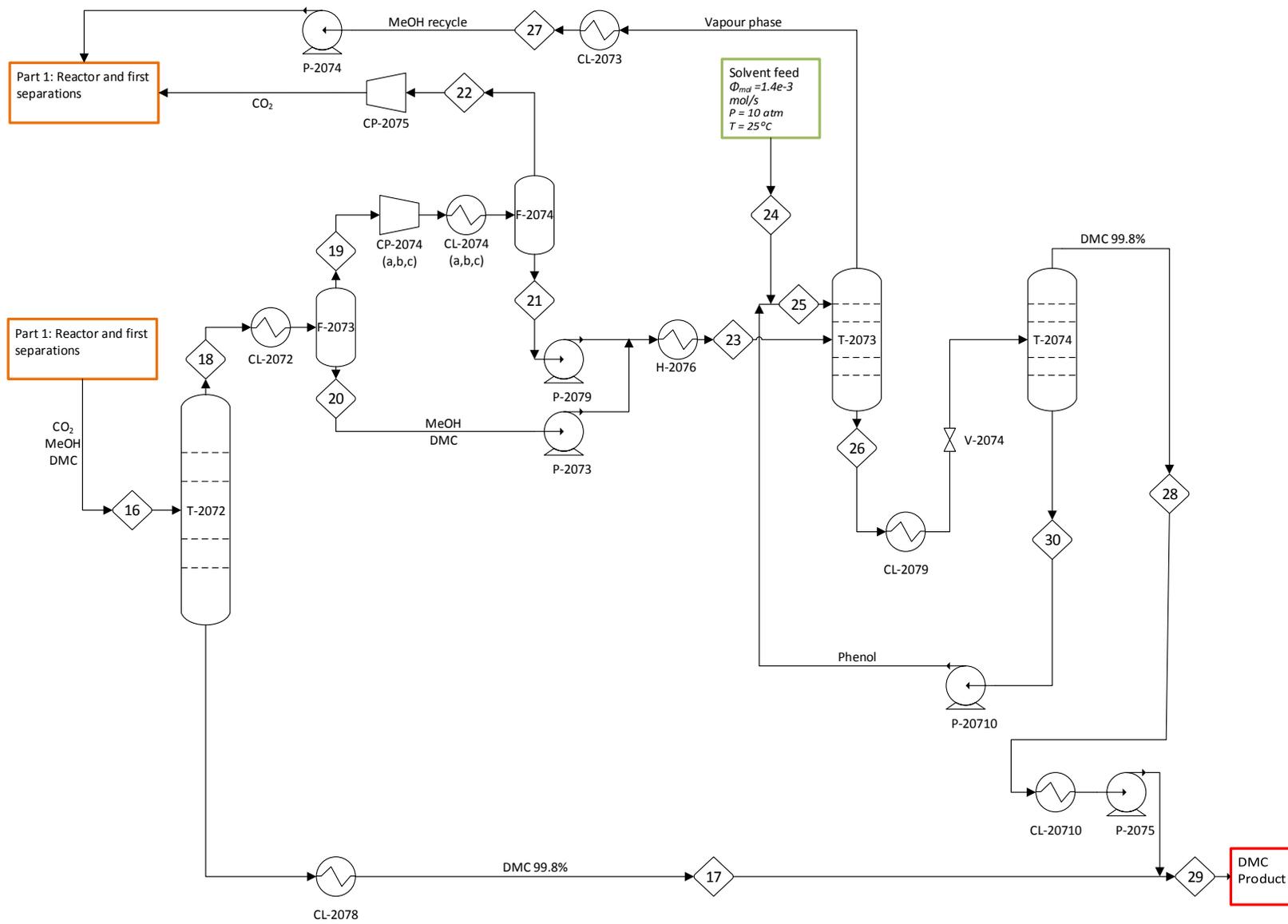


Figure 95: Index flowsheet - part three

## Appendix G Chapter 7 - Process flow diagram

### Appendix G.1. UNISIM mass balance (energy flow included)

Name	1a	1b	1c	1d	1e	1f	1g	1h	2a	2b	3a	3b	4a	4b	5a	5b	6a
Temperature (C)	25.0	127.8	40.0	145.5	40.0	144.0	95.0	122.1	25.0	26.4	25.0	28.3	45.8	147.0	30.7	150.0	122.6
Pressure (kPa)	100	300	280	830	810	2350	2330	3020	100	3020	100	3020	3020	3000	3020	3000	3020
Vapour Fraction	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	1.00	1.00	0.00	0.00	0.00
Mass Flow (kg/h)	2.75E+04	4.01E+04	4.01E+04	5.21E+01	5.21E+01	1.22E+05	1.22E+05	4.32E+04	4.32E+04	7.49E+04							
Molar Flow (kmole/h)	6.24E+02	1.25E+03	1.25E+03	5.00E-01	5.00E-01	2.77E+03	2.77E+03	1.35E+03	1.35E+03	7.20E+02							
Energy Flow (kJ/h)	-2.46E+08	-2.43E+08	-2.45E+08	-2.43E+08	-2.46E+08	-2.43E+08	-2.44E+08	-2.44E+08	-3.00E+08	-3.00E+08	7.90E+04	7.92E+04	-1.09E+09	-1.07E+09	-3.22E+08	-3.01E+08	1.23E+08
<i>Composition</i>																	
Methanol (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1252.00	1252.00	0.00	0.00	8.55	8.55	1346.08	1346.08	0.00
DMC (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.66	7.66	0.95	0.95	0.00
H2O (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phenol (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO2 (kmole/h)	624.00	624.00	624.00	624.00	624.00	624.00	624.00	624.00	0.00	0.00	0.00	0.00	2750.97	2750.97	0.43	0.43	0.00
2-cyanopyridine (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.50	0.50	0.00	0.00	0.00	0.00	719.82
2-picolinamide (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Name	6b	7.1	7.2	7a	7b	7c	8	8a	8b	8c	8d	9a	9b	10	11	12a	12b
Temperature (C)	150.0	120.0	120.0	120.1	120.1	120.0	120.0	117.2	150.0	118.3	150.0	120.0	20.0	20.0	20.0	20.0	21.2
Pressure (kPa)	3000	3000	3000	3000	3000	3000	3000	1000	980	120	100	3000	2980	2980	2980	2980	3020
Vapour Fraction	0.00	1.00	0.00	0.65	0.65	0.62	0.00	0.03	0.04	0.18	0.38	1.00	0.93	0.00	1.00	1.00	1.00
Mass Flow (kg/h)	7.49E+04	1.02E+05	1.38E+05	2.40E+05	2.40E+05	2.40E+05	1.38E+05	1.38E+05	1.38E+05	1.38E+05	1.38E+05	1.02E+05	1.02E+05	1.11E+04	9.13E+04	9.13E+04	9.13E+04
Molar Flow (kmole/h)	7.20E+02	2.22E+03	1.36E+03	4.83E+03	4.84E+03	3.59E+03	1.36E+03	1.36E+03	1.36E+03	1.36E+03	1.36E+03	2.22E+03	2.22E+03	1.55E+02	2.07E+03	2.07E+03	2.07E+03
Energy Flow (kJ/h)	1.26E+08	-8.37E+08	-2.53E+08	-1.25E+09	-1.25E+09	-1.09E+09	-2.53E+08	-2.53E+08	-2.47E+08	-2.47E+08	-2.33E+08	-8.37E+08	-8.51E+08	-3.72E+07	-8.14E+08	-8.14E+08	-8.14E+08
<i>Composition</i>																	
Methanol (kmole/h)	0.00	38.06	64.89	1354.62	1354.63	102.95	64.89	64.89	64.89	64.89	64.89	38.06	38.06	30.48	7.58	7.58	7.58
DMC (kmole/h)	0.00	105.94	528.53	8.61	8.62	634.46	528.53	528.53	528.53	528.53	528.53	105.94	105.94	98.62	7.32	7.32	7.32
H2O (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phenol (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO2 (kmole/h)	0.00	2078.48	48.91	2751.40	2753.24	2127.40	48.91	48.91	48.91	48.91	48.91	2078.48	2078.48	25.19	2053.29	2053.29	2053.29
2-cyanopyridine (kmole/h)	719.82	0.65	93.76	719.82	720.25	94.41	93.76	93.76	93.76	93.76	93.76	0.65	0.65	0.65	0.00	0.00	0.00
2-picolinamide (kmole/h)	0.00	0.28	625.56	0.00	0.00	625.84	625.56	625.56	625.56	625.56	625.56	0.28	0.28	0.28	0.00	0.00	0.00

Name	12c	12d	13	14a	14b	14c	14d	15a	15b	15c	16	17a	17b	18a	18b	19a	19b
Temperature (C)	50.0	24.3	20.0	51.3	124.3	65.0	150.0	223.2	223.3	120.0	87.9	95.5	40.0	52.2	20.0	20.0	119.6
Pressure (kPa)	2960	120	2980	30	65	45	120	50	140	120	120	120	100	100	80	80	240
Vapour Fraction	0.06	0.18	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00	0.89	0.00	0.00	1.00	0.45	1.00	1.00
Mass Flow (kg/h)	1.11E+04	1.11E+04	0.00E+00	5.13E+04	5.13E+04	5.13E+04	5.13E+04	8.67E+04	8.67E+04	8.67E+04	6.23E+04	5.33E+04	5.33E+04	9.06E+03	9.06E+03	4.02E+03	4.02E+03
Molar Flow (kmole/h)	1.55E+02	1.55E+02	0.00E+00	6.36E+02	6.36E+02	6.36E+02	6.36E+02	7.26E+02	7.26E+02	7.26E+02	7.91E+02	5.91E+02	5.91E+02	2.00E+02	2.00E+02	9.05E+01	9.05E+01
Energy Flow (kJ/h)	-3.67E+07	-3.67E+07	0.00E+00	-1.18E+08	-1.16E+08	-1.18E+08	-1.15E+08	-1.06E+08	-1.06E+08	-1.19E+08	-1.52E+08	-1.14E+08	-1.17E+08	-5.32E+07	-5.75E+07	-3.23E+07	-3.20E+07
<i>Composition</i>																	
Methanol (kmole/h)	30.48	30.48	0.00	64.84	64.84	64.84	64.84	0.05	0.05	0.05	95.32	0.13	0.13	95.19	95.19	12.49	12.49
DMC (kmole/h)	98.62	98.62	0.00	522.19	522.19	522.19	522.19	6.34	6.34	6.34	620.80	590.32	590.32	30.48	30.48	4.08	4.08
H2O (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phenol (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO2 (kmole/h)	25.19	25.19	0.00	48.91	48.91	48.91	48.91	0.00	0.00	0.00	74.10	0.00	0.00	74.10	74.10	73.96	73.96
2-cyanopyridine (kmole/h)	0.65	0.65	0.00	0.00	0.00	0.00	0.00	93.76	93.76	93.76	0.65	0.65	0.65	0.00	0.00	0.00	0.00
2-picolinamide (kmole/h)	0.28	0.28	0.00	0.00	0.00	0.00	0.00	625.56	625.56	625.56	0.28	0.28	0.28	0.00	0.00	0.00	0.00
Name	19c	19d	19e	19f	19g	20a	20b	21a	21b	22a	22b	23a	23b	24	25	26a	26b
Temperature (C)	45.0	121.9	60.0	132.5	20.0	20.0	20.6	20.0	20.0	20.0	123.6	20.6	125.0	25.0	188.2	244.9	160.0
Pressure (kPa)	220	500	480	1020	1000	80	1040	1000	1040	1000	3020	1040	1020	1020	1020	1020	1000
Vapour Fraction	1.00	1.00	1.00	1.00	0.83	0.00	0.00	0.00	0.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Flow (kg/h)	4.02E+03	4.02E+03	4.02E+03	4.02E+03	4.02E+03	5.03E+03	5.03E+03	7.18E+02	7.18E+02	3.30E+03	3.30E+03	5.75E+03	5.75E+03	0.00E+00	6.22E+03	8.85E+03	8.85E+03
Molar Flow (kmole/h)	9.05E+01	9.05E+01	9.05E+01	9.05E+01	9.05E+01	1.09E+02	1.09E+02	1.55E+01	1.55E+01	7.50E+01	7.50E+01	1.25E+02	1.25E+02	0.00E+00	6.60E+01	9.54E+01	9.54E+01
Energy Flow (kJ/h)	-3.22E+07	-3.20E+07	-3.22E+07	-3.19E+07	-3.29E+07	-2.52E+07	-2.52E+07	-3.63E+06	-3.63E+06	-2.93E+07	-2.90E+07	-2.88E+07	-2.73E+07	0.00E+00	-7.96E+06	-1.22E+07	-1.38E+07
<i>Composition</i>																	
Methanol (kmole/h)	12.49	12.49	12.49	12.49	12.49	82.70	82.70	11.52	11.52	0.96	0.96	94.22	94.22	0.00	0.00	0.15	0.15
DMC (kmole/h)	4.08	4.08	4.08	4.08	4.08	26.41	26.41	3.73	3.73	0.35	0.35	30.14	30.14	0.00	0.07	29.25	29.25
H2O (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phenol (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	65.98	65.98	65.98
CO2 (kmole/h)	73.96	73.96	73.96	73.96	73.96	0.14	0.14	0.28	0.28	73.67	73.67	0.43	0.43	0.00	0.00	0.00	0.00
2-cyanopyridine (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-picolinamide (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Name	26c	27a	27b	27c	28a	28b	28c	29	30a	30b	30c	31a	31b	32	32.1	32.2	33
Temperature (C)	147.5	136.5	85.0	86.0	88.8	40.0	40.0	40.0	187.7	187.7	188.2	120.0	120.0	120.0	120.0	120.0	120.0
Pressure (kPa)	120	1000	980	3020	100	80	100	100	120	120	1020	120	120	120	120	120	120
Vapour Fraction	0.07	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	1.00
Mass Flow (kg/h)	8.85E+03	3.12E+03	3.12E+03	3.12E+03	2.63E+03	2.63E+03	2.63E+03	5.59E+04	6.22E+03	6.22E+03	6.22E+03	8.67E+04	8.67E+04	8.67E+04	0.00E+00	8.67E+04	1.18E+04
Molar Flow (kmole/h)	9.54E+01	9.55E+01	9.55E+01	9.55E+01	2.93E+01	2.93E+01	2.93E+01	6.21E+02	6.60E+01	6.60E+01	6.60E+01	7.26E+02	7.26E+02	1.35E+03	0.00E+00	1.35E+03	6.32E+02
Energy Flow (kJ/h)	-1.38E+07	-1.88E+07	-2.22E+07	-2.22E+07	-5.71E+06	-5.82E+06	-5.82E+06	-1.23E+08	-7.97E+06	-7.97E+06	-7.96E+06	-1.19E+08	-1.19E+08	-5.22E+07	0.00E+00	-5.22E+07	-1.50E+08
<i>Composition</i>																	
Methanol (kmole/h)	0.15	94.08	94.08	94.08	0.15	0.15	0.15	0.28	0.00	0.00	0.00	0.05	0.05	0.05	0.00	0.05	0.05
DMC (kmole/h)	29.25	0.95	0.95	0.95	29.19	29.19	29.19	619.51	0.07	0.07	0.07	6.34	6.34	6.34	0.00	6.34	6.34
H2O (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	625.56	0.00	625.56	625.56
Phenol (kmole/h)	65.98	0.00	0.00	0.00	0.01	0.01	0.01	0.01	65.98	65.98	65.98	0.00	0.00	0.00	0.00	0.00	0.00
CO2 (kmole/h)	0.00	0.43	0.43	0.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-cyanopyridine (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.65	0.00	0.00	0.00	93.76	93.76	719.32	0.00	719.32	0.00
2-picolinamide (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00	625.56	625.56	0.00	0.00	0.00	0.00

Name	34	35a	35b	35c	36a	36b
Temperature (C)	120.0	120.0	120.0	120.0	120.0	122.7
Pressure (kPa)	120	120	140	140	120	3020
Vapour Fraction	0.00	0.00	0.00	0.00	0.00	0.00
Mass Flow (kg/h)	7.49E+04	0.00E+00	0.00E+00	0.00E+00	7.49E+04	7.49E+04
Molar Flow (kmole/h)	7.19E+02	0.00E+00	0.00E+00	0.00E+00	7.19E+02	7.19E+02
Energy Flow (kJ/h)	1.23E+08	0.00E+00	0.00E+00	0.00E+00	1.23E+08	1.23E+08
<i>Composition</i>						
Methanol (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00
DMC (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00
H2O (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00
Phenol (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00
CO2 (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00
2-cyanopyridine (kmole/h)	719.32	0.00	0.00	0.00	719.32	719.32
2-picolinamide (kmole/h)	0.00	0.00	0.00	0.00	0.00	0.00

## Appendix H Chapter 8 - P&ID

### Appendix H.1. Process control

In this appendix an extended derivation is given for the design of the process control set up of the different unit operations and for the total process. For every section the same steps are taken to get the control set up. First, a block diagram is made, with the control variable, controlled variable and disturbances. Then the controllers are identified in the process flow diagram and valves are placed. If necessary, a table is made with the influences of the control variable on the controlled variables and finally the control scheme is completed. A work diagram is given in Figure 10 at page 42.

#### H.1.1. Flash vessel

The process control set up of the flash vessels F-2071, F-2072, F-2072 and F-2074 is designed in this section, starting with the block diagram (Figure 96). Here the goal is to control the liquid level inside the vessel. No buffer is placed before the vessel, so the inflow is determined by the process and cannot be controlled. Also the temperature and pressure are disturbances which are determined by the process. The outflow of liquid is a control variable and therefore the outflow of gas is set, a measurable non-controlled variable. This results in the presented block diagram.

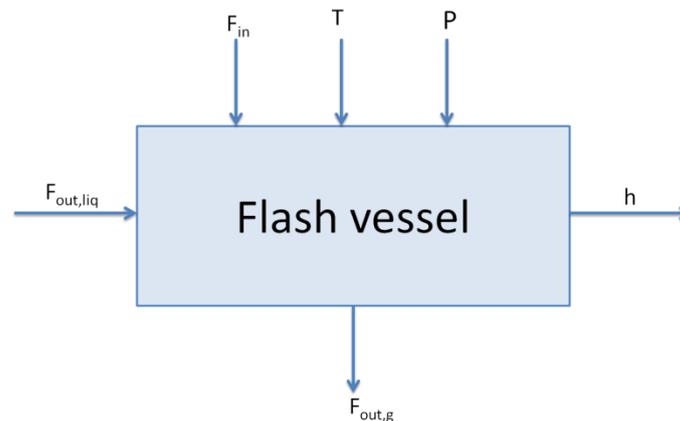


Figure 96: Block diagram for process control of the flash vessels

The controlled variable is the liquid level inside the flash vessel, therefore a level controller is needed. The control variable is the outflow of liquid from the flash vessel. This can be done by installing a valve. Also the disturbances and non-controlled variables are shown in Figure 97.

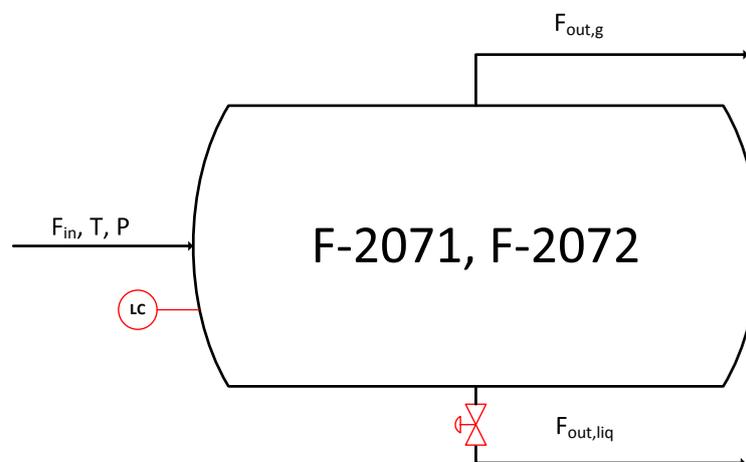


Figure 97: Flash vessel with the controllers and valves

Then the controlled variables and control variables are linked. In this case it is quite easy, there is only one possibility. However, it must be checked if it is a valid combination. In this case it is, the liquid outflow can control the liquid level inside the vessel. The complete process control scheme is shown in Figure 98.

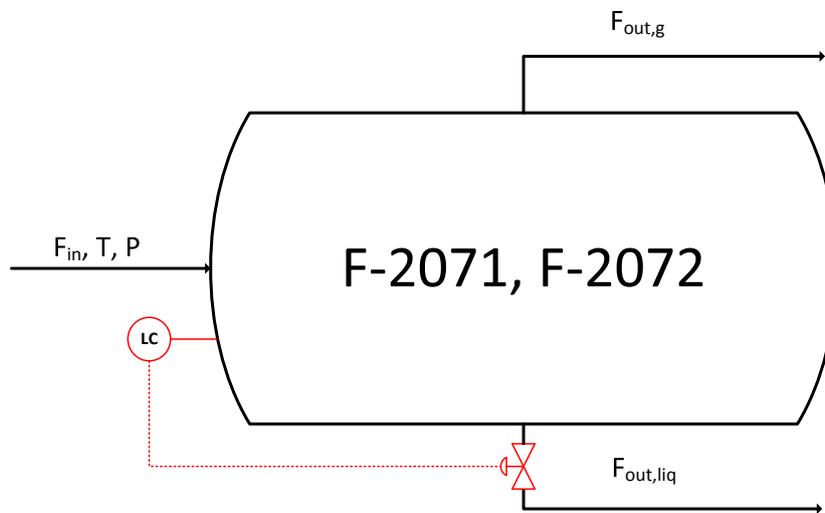


Figure 98: Complete control set up for a flash vessel

#### H.1.2. Heater

The heaters in the process (H-2071, H-2072, H-2073, H2074, H-2075 and H-2076) all have the same goal. This is to heat up the feed stream to a desired temperature. The load is determined by the rest of the process and so is the inlet temperature. In this case the controlled variable is the temperature of the outlet stream, which needs to be heated. Steam is used to heat up the feed and condensed water flows out the system. The driving force is the temperature difference between steam and fluid that is heated. The temperature of steam depends on its pressure and the pressure is again a function of the amount of steam fed to the heater.

On the steam side, always a certain level of condensed water needs to be present. A steam trap is suitable to realize this and it is self controlling. As a result, the outflow of water is set by the steam trap and the pressure inside the reactor by the amount of steam. The block diagram that results from this is shown in Figure 99.

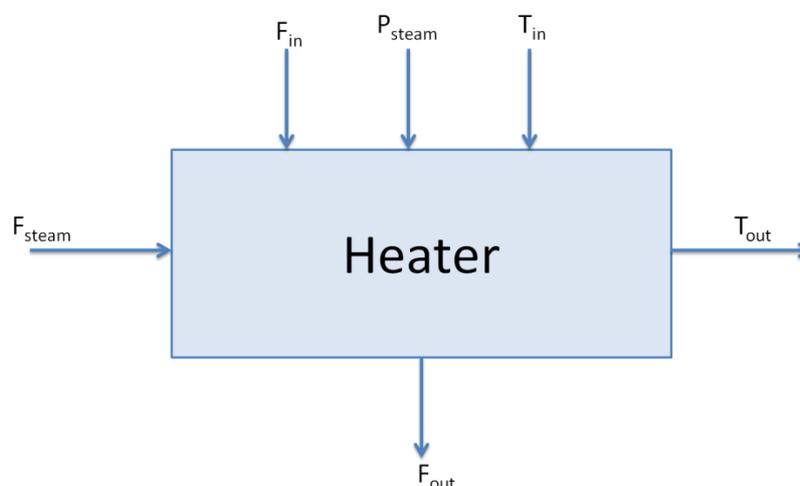


Figure 99: Block diagram for process control set up of a heater

For the control scheme, a steam trap is needed in the outflow of condensate and a valve is needed to control the amount of steam that will enter the heater. The goal is heat up the stream to the desired temperature, so a temperature controller is installed at the outlet. Everything together results in Figure 100.

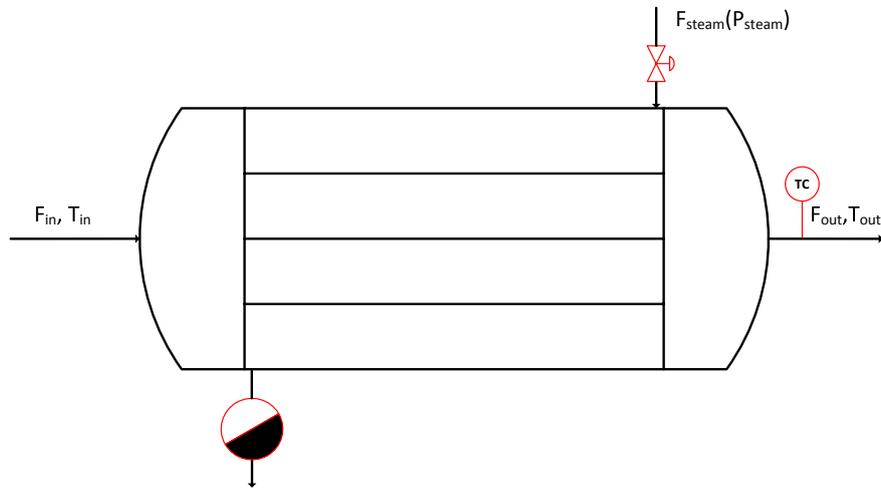


Figure 100: Valves and controllers for a heater

As stated before, the temperature difference between steam and fluid will determine the temperature of the fluid at the outlet. Eventually this is a function of the amount of steam entering the heater. Therefore, it is possible to connect the valve and the temperature controller. The total control scheme is given in Figure 101.

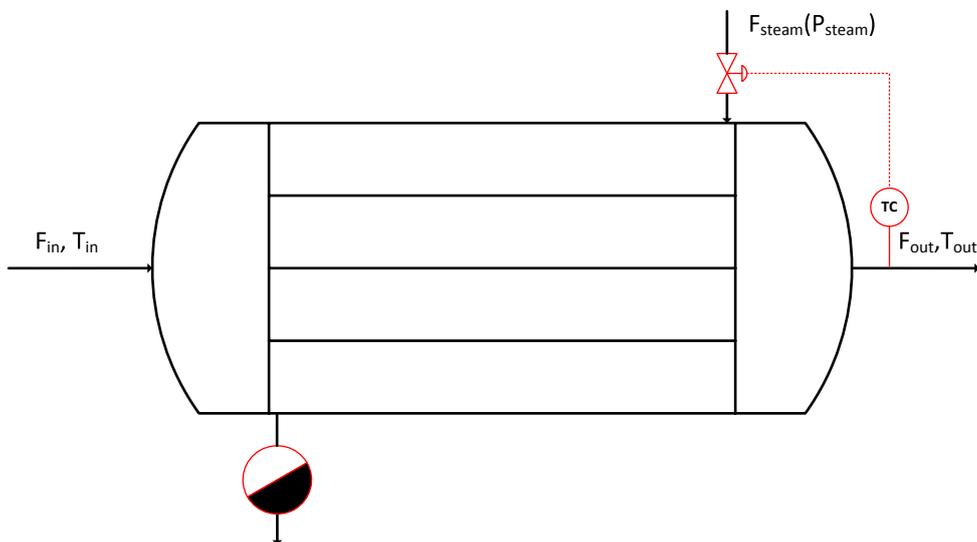


Figure 101: Complete process control set up for a heater

### H.1.3. Cooler

A cooler looks pretty similar to a heater. Only now there is cooling water entering the heat exchanger and hot water or steam is leaving on the other side. The goal is also similar, to cool a stream from a certain temperature to a set temperature. The block diagram is given in Figure 102.

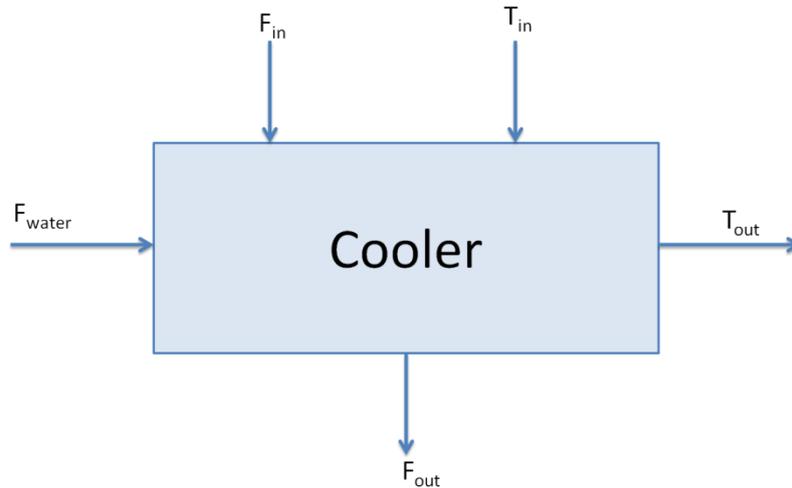


Figure 102: Process control block diagram for a cooler

A temperature controller is needed in the outlet of the fluid. The control variable is the inlet of cooling water, so here a valve is installed (Figure 103). By increasing the amount of cooling water, the temperature rise in cooling water will decrease, therefore the overall driving force is increased and the outlet temperature of the cooled fluid is decreased. So, it is possible to control the temperature by changing the amount of cooling water (Figure 104). This is valid for all the coolers in the system (CL-2071, CL-2072, CL-2073, CL-2074 and CL-2075).

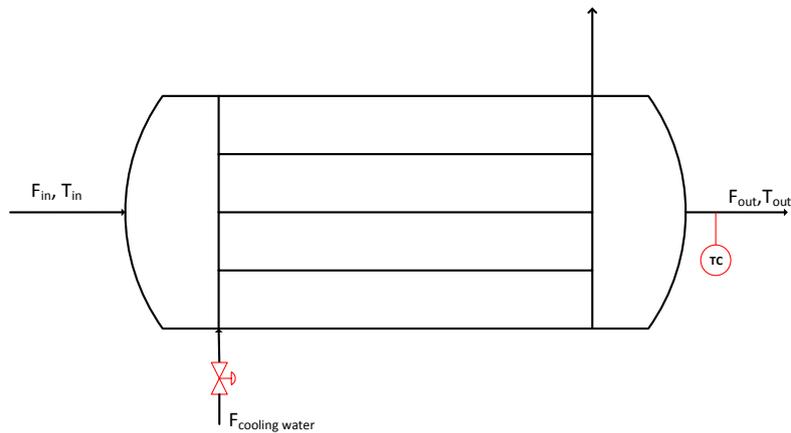


Figure 103: A cooler with process control equipment installed

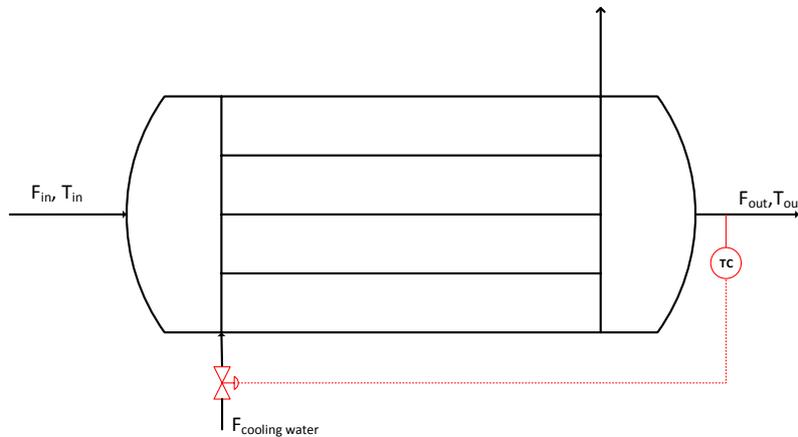


Figure 104: Complete process control set up for a cooler

#### H.1.4. Distillation column

There are multiple distillation columns in the process and all the columns have different goals. Thus, the control set up might differ from column to column. For all columns, a control set up is designed in this section.

##### H.1.4.1. DMC/methanol separation (T-2072)

The purpose of this column is to separate DMC and methanol. In the bottom of the column DMC should be obtained with the desired purity of 99.8 wt%. In the top, the mixture reaches azeotropic conditions. With extractive distillation this mixture is separated in a different column, the control scheme for this column will be designed in section H.1.4.2.

The block diagram for this distillation column is shown in Figure 105. All conditions for the feed are determined by the units in front, no buffers are used and therefore these are all disturbances. The control variables are the flows involved in the system: condenser, reboiler, bottom, distillate and reflux. The goal is to obtain a certain purity in the bottom and needs to be controlled. Other controlled variables are the levels in the condenser and in the bottom of the column and the pressure and temperature in the column.

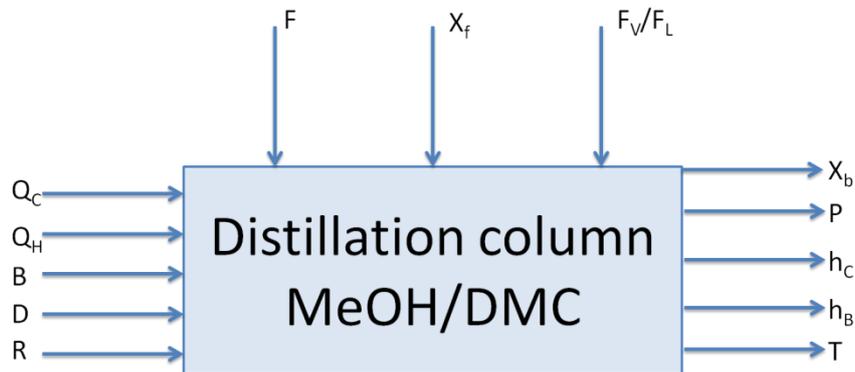


Figure 105: Block diagram for the process control set up of T-2071

Valves are installed in every adjustable flow and controllers placed for the controlled variables. The kind of controllers is pretty obvious and no further explanation will be needed. This is shown in Figure 106. The top product is obtained as a vapour, due to a little amount of CO<sub>2</sub> that is still present in the column. In this way the temperature of the condenser does not need to be extremely low in order to liquefy the CO<sub>2</sub>.

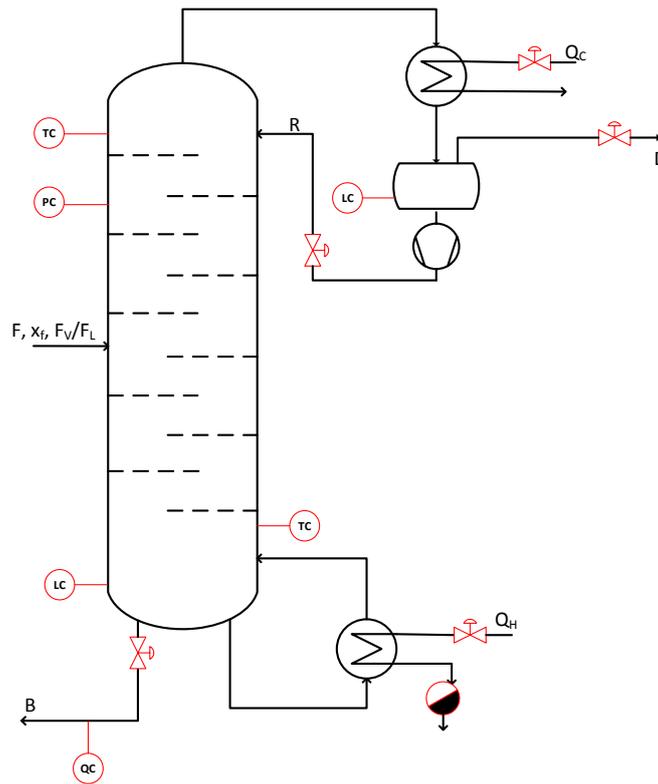


Figure 106: Controllers and valves for T-2072

To determine which control variable is attached to which controlled variable, a table is made with the influences on each other (Table 46). The chosen combinations are highlighted.

Table 46: Influences of the control variables on the controlled variables

	P	L <sub>T</sub>	L <sub>B</sub>	T	X <sub>B</sub>
D	+	-	-	-	-
B	-	-	+	-	-
Q <sub>H</sub>	+	+ -	+ -	+	+
Q <sub>C</sub>	+	+	+ -	+	+ -
R	+ -	+	+ -	+	-

The level controllers in the top and bottom are controlled by the reflux and bottom flows respectively. However, in some cases this is not completely possible and also a fraction control needs to be present. These controller(s) are also present in the process control set up shown in Figure 107. Quality control is usually not possible in situ, therefore the purity in the bottom is also related to the temperature close to the bottom.

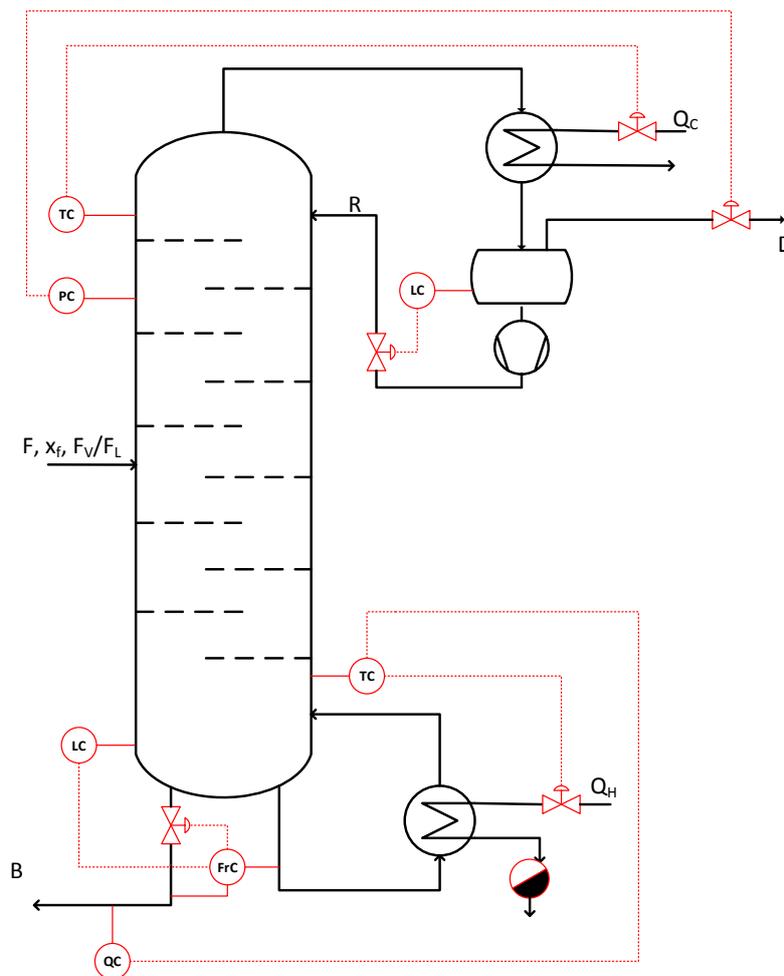


Figure 107: Complete control set up for T-2072

#### H.1.4.2. Separating dehydrating and derivatives (T-2071)

The liquid stream from the first flash vessel contains DMC as well as dehydrating agent. In this column, the 2-cyanopyridine and 2-picolinamide are collected at the bottom and a DMC rich stream is obtained at the top. Besides DMC also significant amounts of methanol and CO<sub>2</sub> are present in the top, therefore the top product is obtained in the vapour phase. The pressure in the column is below atmospheric, in order to decrease the required temperature, so the reboiler can be operated with steam.

Most important is that there is no DMC leaving at the bottom of the column, because the condenser operates at a very low temperature it is unlikely that any dehydrating related compounds will be present in the top.

With the top product being a vapour and a quality constraint in the bottom stream, the process control set up is exactly the same as for the methanol/DMC column in the previous section.

#### H.1.4.3. Extractive distillation column (T-2073, T-2074)

With extractive distillation, the azeotrope in the DMC/methanol mixture is overcome. This column handles the mixture that is obtained at the top of the previous distillation column. When a high boiling solvent is used, the goal of this column is to obtain pure methanol for the recycle and to recover as much DMC as possible in the bottom. If a low boiling solvent is used, the goal is to obtain DMC with the specified purity of 99.8 wt%. In this case, phenol is used as solvent, which is a high boiling solvent. After the extractive distillation column an additional distillation column is placed to recover the solvent and obtain pure DMC. The DMC product is then mixed with the DMC from the first column and the

solvent is recycled to the extractive distillation column. DMC should be 99.8 wt% pure and also the solvent should be very pure. This is because the solvent will enter the extractive distillation column at one of the top trays where there should be a methanol rich environment. Feeding DMC to the column at this place is very unfavourable for the methanol purity in the distillate. The methanol is recycled to the reactor and therefore it is desired to have as less DMC as possible in it. So, there are quality constrains at both the bottom and the distillate. These columns are combined in this section, because they are directly connected with the phenol recycle. The block diagram is shown in Figure 108. There can only be a valve in one of the bottom streams, because there is a limited amount of solvent in the system and therefore the level in column one depends on the level in column two. Then in the other stream is a valve controlling the amount of solvent entering one of the columns. In this case the choice is made to control the amount of solvent entering and leaving the extractive distillation column.

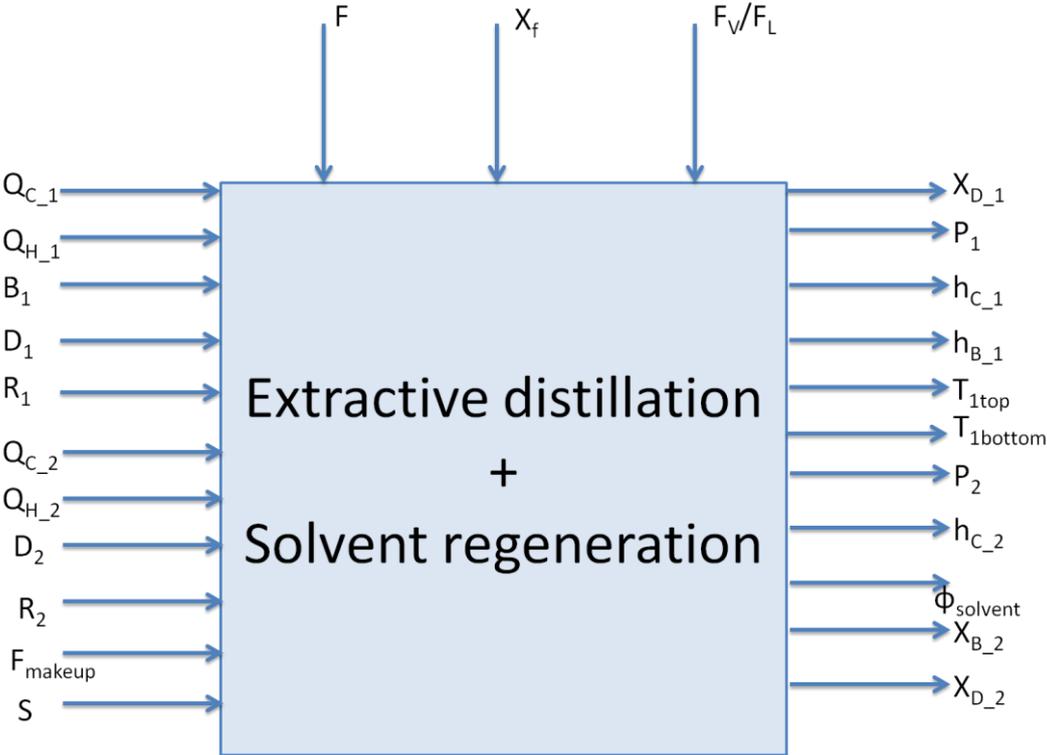


Figure 108: The combined block diagram for the extractive distillation column and solvent regeneration column (1 refers to the extractive distillation column and 2 refers to the solvent regeneration column)

With this block diagram, the valves and controllers are placed in the process flow diagram. A flow controller is placed, because a fixed amount of fresh solvent should enter the column. Figure 109 gives the complete flow diagram with controllers and valves.

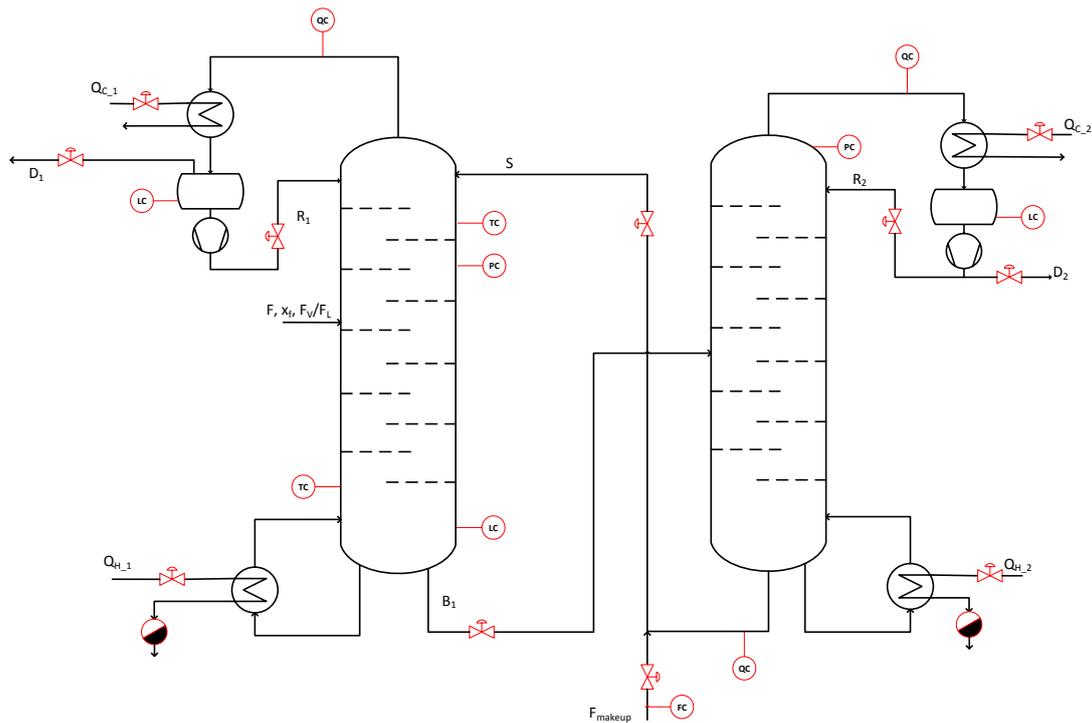


Figure 109: Control and controlled variables for the extractive distillation column and solvent regeneration column

In order to connect the controlled variables with the control variables, a table with the influences on each other is set up (Table 47). In green the chosen combinations are indicated and finally this is translated into a complete control set up.

Table 47: Influences of control variable on the controlled variables for an extractive distillation system

	$X_{D_1}$	$P_1$	$h_{C_1}$	$h_{B_1}$	$T_{1top}$	$T_{1bottom}$	$P_2$	$h_{C_2}$	$\phi_{solvent}$	$X_{B_2}$	$X_{D_2}$
$Q_{c_1}$	+	+	+	-	+	-	-	-	-	-	-
$Q_{H_1}$	+ -	+	+ -	+	+	+	-	-	-	-	-
$B_1$	-	-	-	+	-	-	+ -	-	-	+ -	+ -
$D_1$	-	+	-	-	+	+ -	-	-	-	-	-
$R_1$	+	+	+	-	+	+ -	-	-	-	-	-
$Q_{c_2}$	-	-	-	-	-	-	+	+	-	+ -	+
$Q_{H_2}$	+ -	+ -	-	-	+ -	-	+	-	-	+	-
$D_2$	-	-	-	-	-	-	-	+	-	-	-
$R_2$	-	-	-	-	-	-	+	+	-	+ -	+
$F_{makeup}$	+	+ -	-	+	+	+ -	-	-	+	+ -	+ -
$S$	+	+ -	-	+ -	+ -	+ -	-	-	-	+ -	+

As the distillate of the extractive distillation column is a vapour, this is very suitable to keep the pressure inside the column at a certain level. The azeotrope prevents the opportunity to obtain pure methanol, the phenol therefore should enable this. Therefore, the amount of solvent fed to the column

is used to control the purity of methanol. The feed of fresh solvent is controlled by a flow controller in the same stream, although a level controller in the regeneration column is placed to indicate the flow controller. All this results in the control scheme in Figure 110.

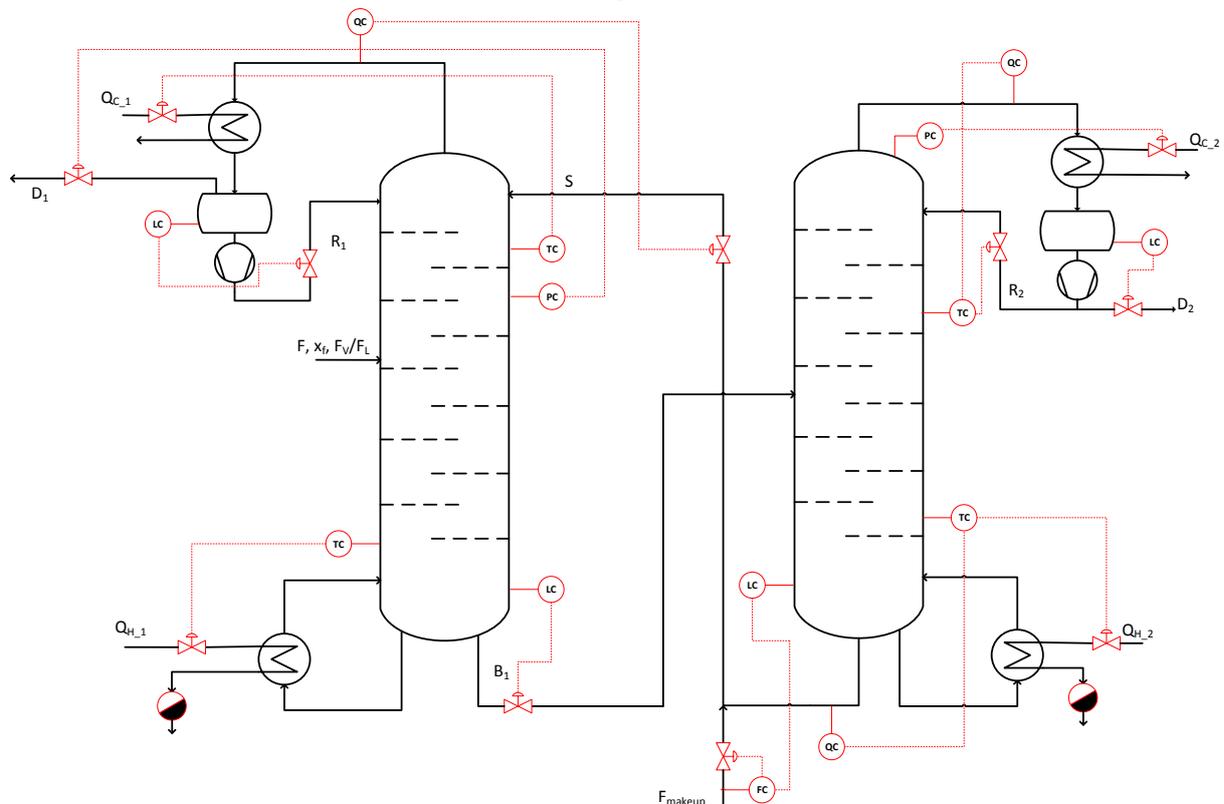


Figure 110: Control scheme for the extractive distillation column

#### H.1.5. Process overall

Finally, for the overall process, a process control set up is designed. For this the process is split in different parts to make it less complicated. These parts can be seen as individual plants and are defined as:

- 4) Reactor and first two flash vessels
- 5) Regeneration of dehydrating agent
- 6) Purification of DMC

##### H.1.5.1. Part one

The first part of the process consists of the reactor in which DMC is formed and the first separation section. After this section, a stream (#16) containing 2-picolinamide and 2-cyanopyridine will go to the regeneration and a stream (#15) with mostly DMC will be purified.

Part one contains one reactor (R-2071), two flash vessels (F-2071 and F-2072) and a distillation column (T-2071). The control schemes for these unit operations are already designed in previous sections. Also for the heaters (H-2071, H-2072, H-2073 and H-2074) and cooler (CL-2071) a control scheme is made.

At first, the valves are placed at the streams entering and leaving the process. Here the feed of methanol, CO<sub>2</sub> and 2-cyanopyridine are not fixed and therefore a control variable. There is one outflow and that is for the CO<sub>2</sub> purge (DMC product is covered in part 3).

There are several parameters, that need to be controlled. Inside the reactor the pressure is fixed at 30 bar and at the inlet of the reactor, the ratio between methanol and dehydrating agent needs to be

kept constant at 0.5. Also the ratio of methanol and CO<sub>2</sub> should be fixed, but this can interfere with the pressure, because CO<sub>2</sub> is the predominant factor for the pressure. As controlling the pressure is more important, this will be the controlled variable. To make sure that the production of DMC is sufficient, the methanol feed needed for this can be calculated. At last the purge factor has to be controlled and a fixed amount of CO<sub>2</sub> needs to be recycled. This leads to a block diagram as shown in Figure 111. A lot of disturbances play a role in this part of the process, the pressure and temperature of the feed may fluctuate a little from time to time and the load of the recycles is set by a different part of the plant.

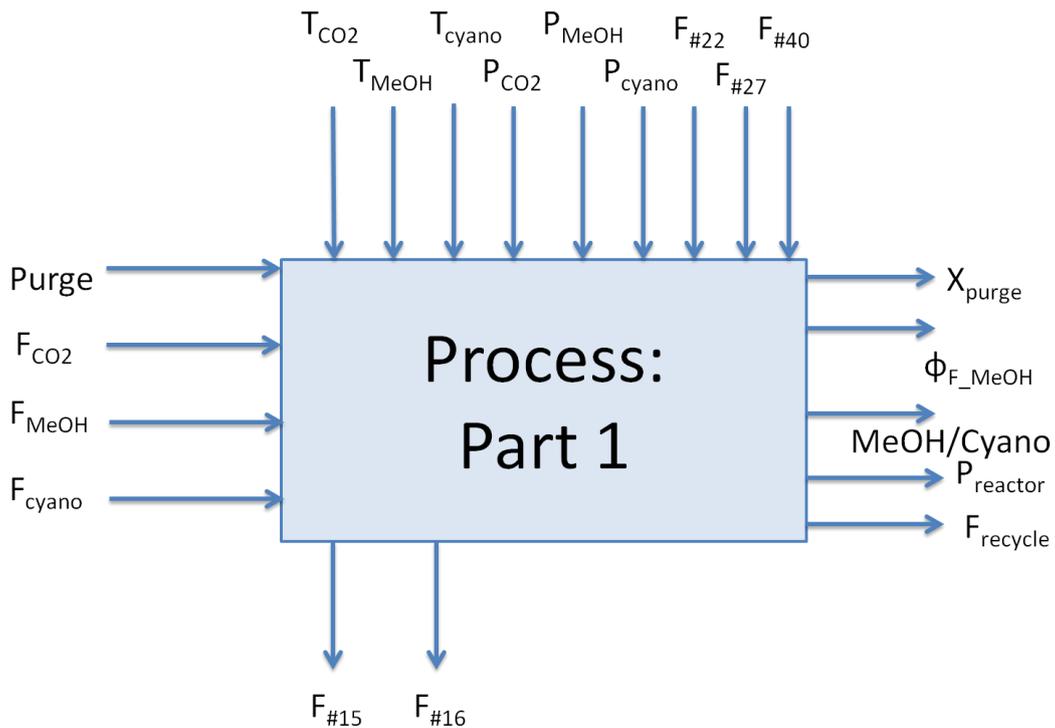


Figure 111: Block diagram for the first part of the process

The control and controlled variables are put into the process. Four valves for the control variables should be installed and two flow controllers, two fraction controllers (for the purge and methanol/agent ratio) and a pressure controller are needed. The flow diagram including the mentioned equipment is shown in Figure 112.

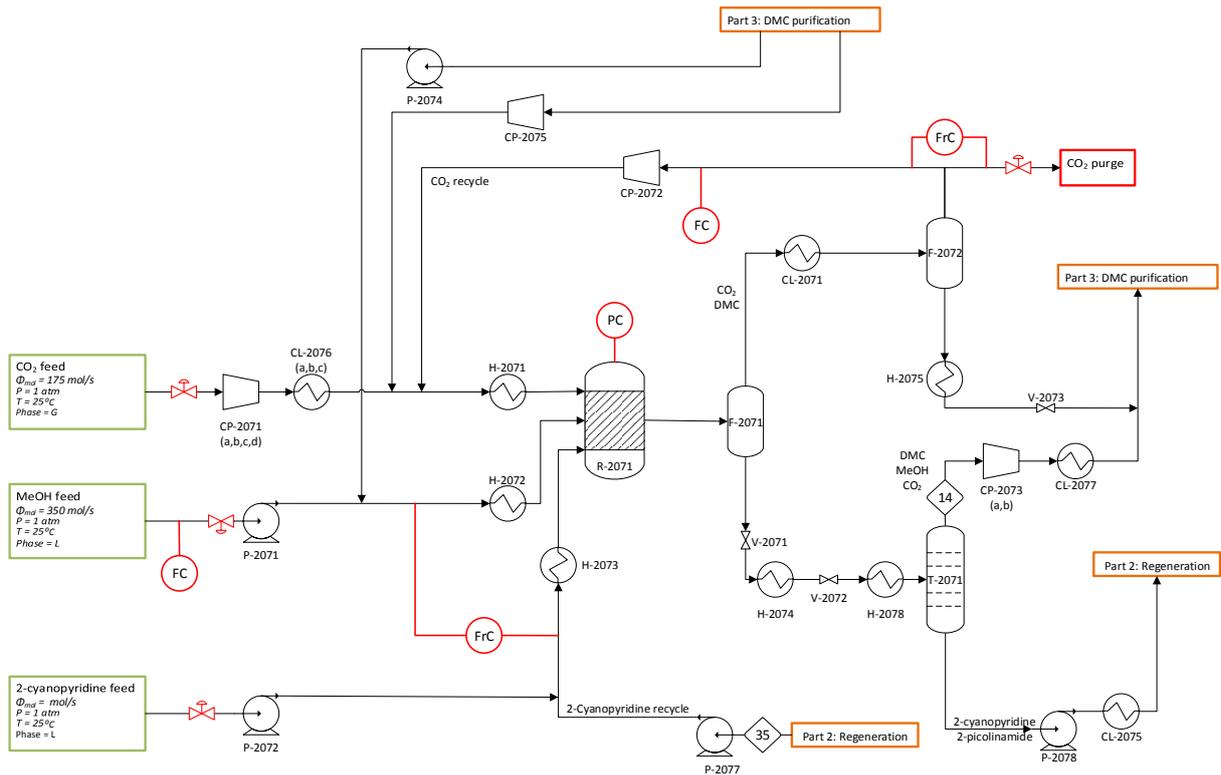


Figure 112: Valves and process controllers in the first part of the process

In the block diagram there are not an equal amount of control and controlled variables. One of the controlled variable cannot be controlled by opening or closing a valve, but is related to the compressor speed. This is the flow of the recycle, and is connected to CP-2072.

A table with the influences of the control variables on the controlled variables is given below. The pressure inside the reactor can be controlled with all the valves, but the CO<sub>2</sub> feed has by far the largest influence. As it is at high pressure, this needs to be controlled very well and a connection to the CO<sub>2</sub> feed is therefore the most logical option. The other connections are self explanatory.

The complete process control set up is given in Figure 115 at page 161.

Table 48: Influences of controlled variables on control variables

	$\phi_{\text{MeOH}}$	MeOH/DHA	P	$X_{\text{purge}}$
$F_{\text{CO}_2}$	+	-	+	-
$F_{\text{MeOH}}$	+	+	+	-
$F_{\text{cyano}}$	-	+	+	-
$P_{\text{CO}_2}$	+	-	+	+

#### H.1.5.2. Part two

The second part is the regeneration of dehydrating agent. This involves a reaction and separation section, but cannot be designed in detail due to lack of information in literature. The control set up for this section is designed as extended as possible.

This part does not have a feed stream that can be tempered with, the only product streams are purges and a recycle of 2-cyanopyridine to the first part of the process. The block diagram is given in Figure 113.

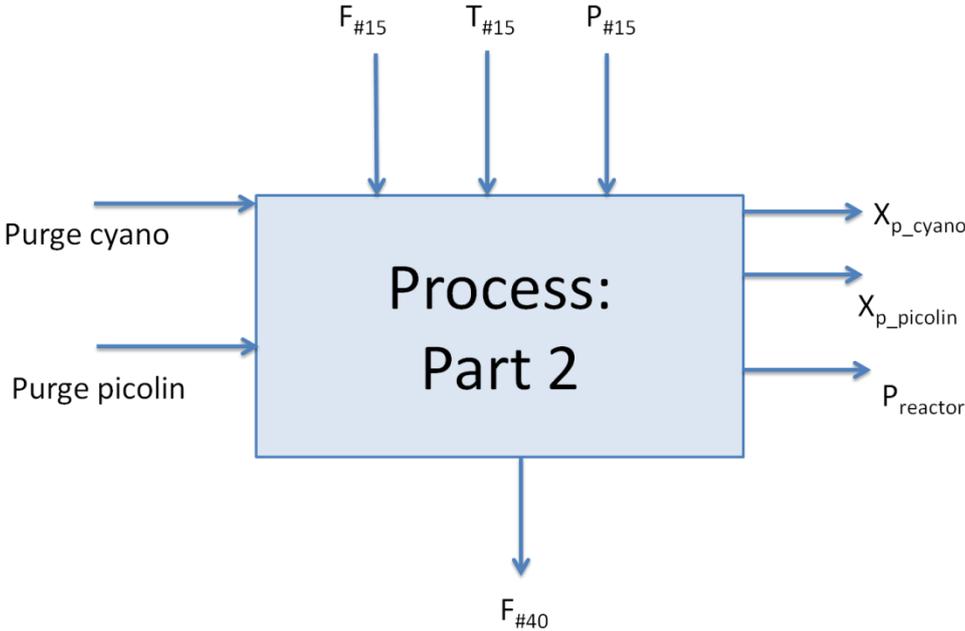


Figure 113: Block diagram for process control of part two

A problem arises from this block diagram. There are three controlled variables, but only two control variables. To overcome this problem, also the pump in the recycle of 2-picolinamide can be used as control variable. These are given in Figure 114.

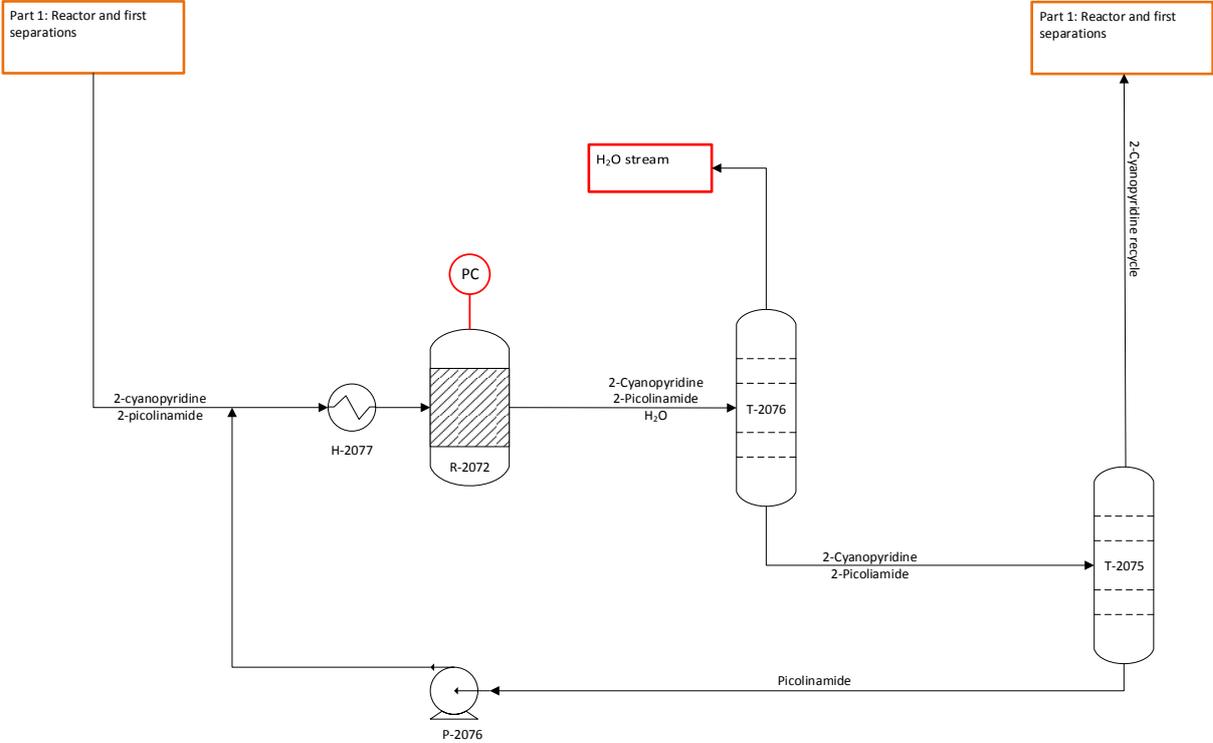


Figure 114: Process controllers and valves for the second part of the process

In this case a table with the mutual influences is not given, because this system is not very complicated. The purge factors can be controlled by the valves in that purge. For the pressure inside the reactor, the pump speed of P-2076 will be used. The result is given in Figure 116 on page 162.

#### *H.1.5.3. Part three*

In the third part of the process a mixture of CO<sub>2</sub>, methanol and DMC is separated. CO<sub>2</sub> and methanol is then recycles to the reactor in part one. In this section there are two flash vessels (F-2073 and F-2074) and three distillation columns (T-2072, T-2073 and T-2074), of which one is an extractive distillation column (T-2073).

The goal of this part is to purify the DMC stream and recycle the separated methanol and CO<sub>2</sub> to the reactor. After designing the process control set up for every single unit, there is no need to put in additional process control equipment.

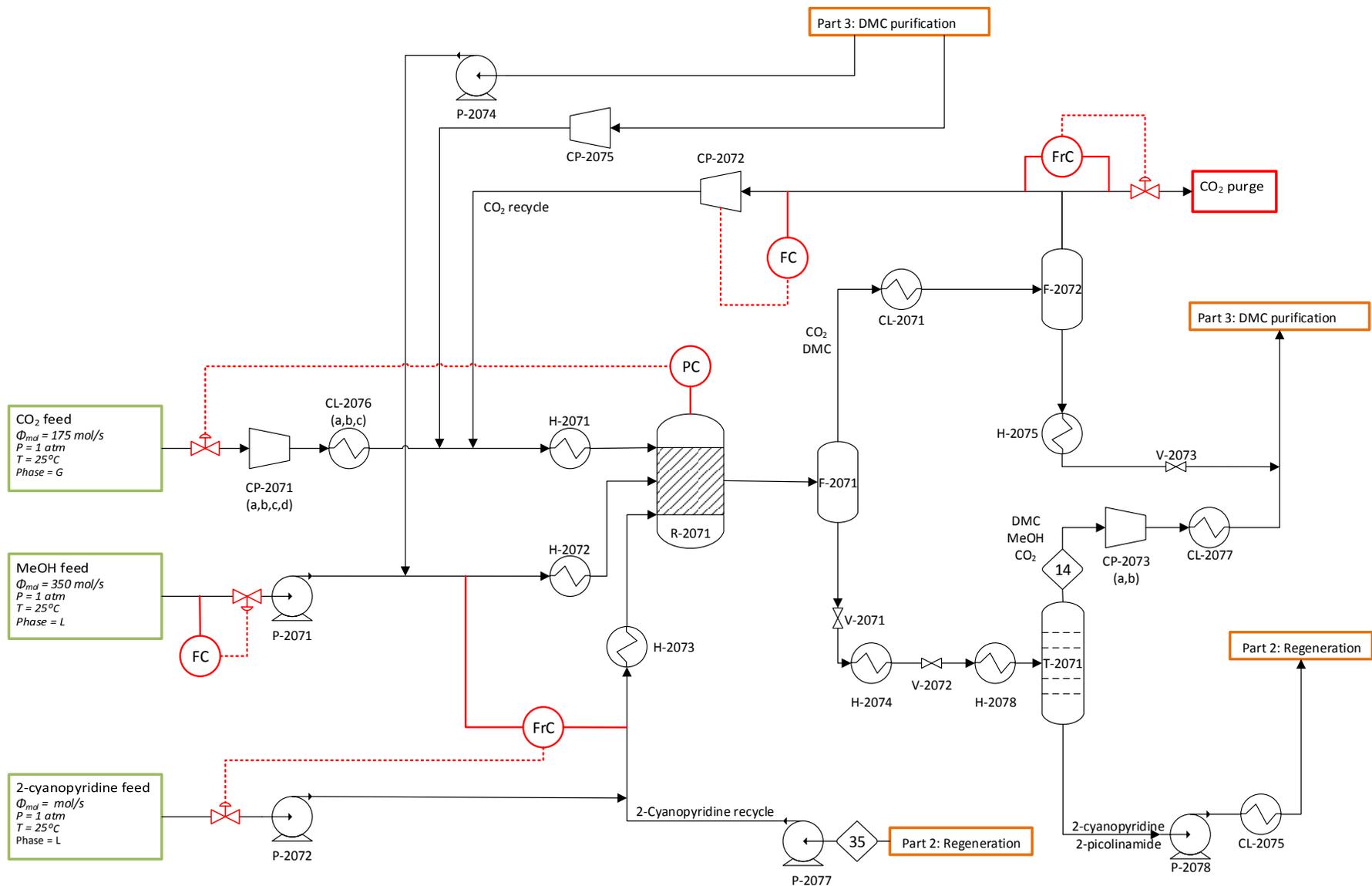


Figure 115: Process control set up for part one of the process

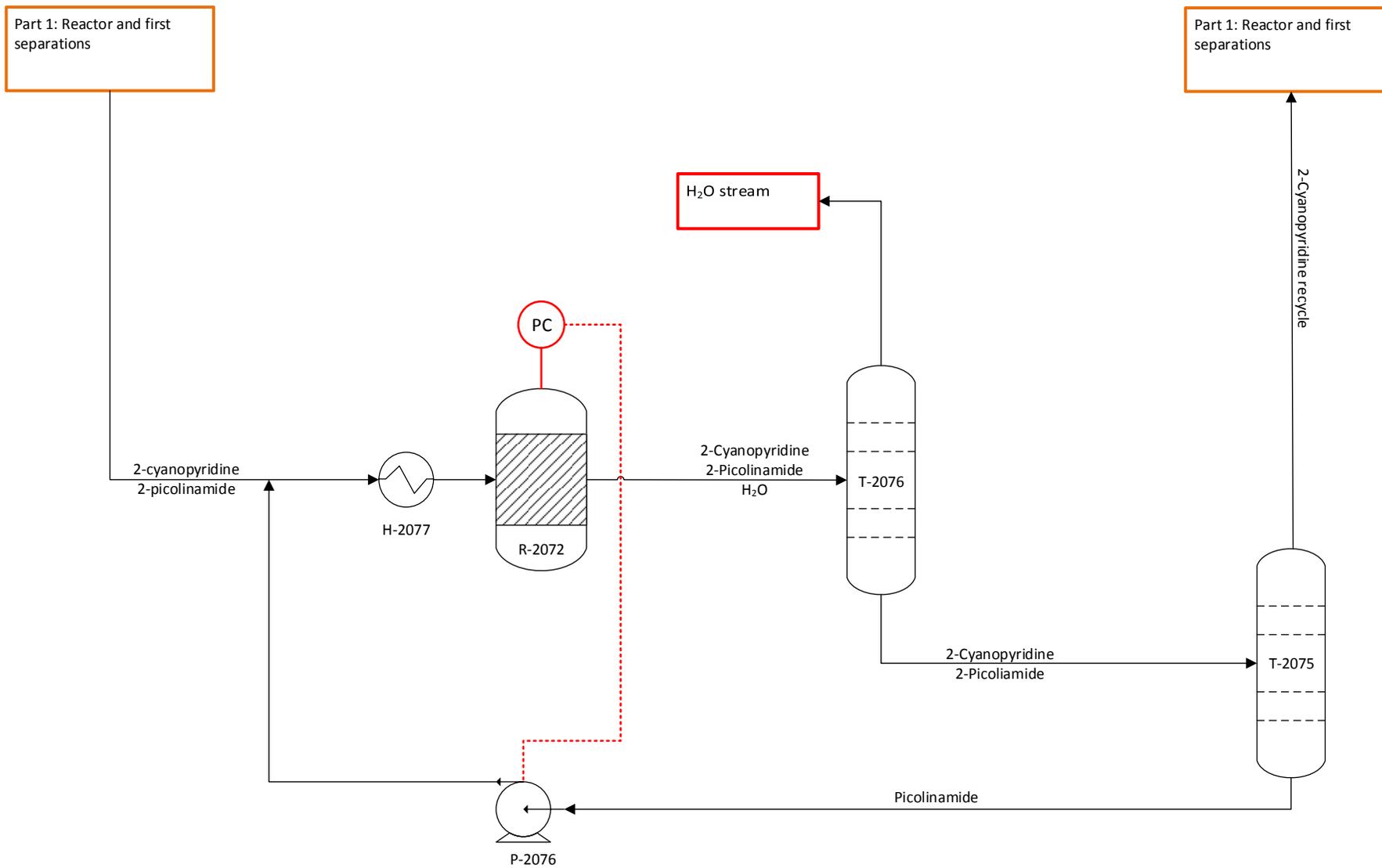


Figure 116: Process control set up for the second part of the process

## Appendix I Chapter 9 - Equipment design

### Appendix I.1. Detailed design of equipment

In this appendix, all equipment in the process is designed. The detail of the design is adjusted to the economics. In other words, the equipment design is such that a good economic evaluation (CAPEX and OPEX) can be made. A list with requirements is given for every piece of equipment, these are the data needed from equipment design for the economic evaluation in chapter 12.

Equipment that is designed are:

- Heat exchanger
- Flash vessel
- Distillation column
- Pump
- Compressor

#### I.1.1. Heat exchanger

A heat integration network was not made. Therefore, all heat exchangers can be substituted by heaters and coolers. Reboilers and condensers are also a type of heat exchangers. To summarize; coolers, heaters, condensers and reboilers are designed in this paragraph. An example is presented for one of the heat exchangers in the process.

The requirements for the economic evaluation are:[80]

- Area [m<sup>2</sup>]
- Type of heat exchanger (U-tube, Fixed head, Floating head, Kettle vaporizer, Double-pipe)
- Tube length [ft]
- Material of shell and tube
- Pressure at shell side [bar]
- Flow of heating/cooling medium [kg/s]

The general equation for the area required for heat transfer is given in (I.24) and for the flow of heat transfer medium (cooling water for a cooler and steam for a heater) in (I.25).[72]

$$Q = UA\Delta T_{LM}F_T \quad (I.24)$$

$$Q = c_p \Phi_m (T_{out} - T_{in}) + \Phi_m \Delta H_{vap} \quad (I.25)$$

The evaporation enthalpy is only added if there is a phase change of the medium. If steam is used for heating purposes, this will be the case. The amount of energy needed to be transferred is adapted from the UNISIM simulation.

For this process, every heat exchanger is assumed to be shell and tube. This is plausible, because there are no extreme pressure or temperature ranges. Also everywhere a U-Tube configuration is assumed at first. When the area is smaller than 19 m<sup>2</sup> a double-pipe heat exchanger can be used.[72]

##### I.1.1.1. Temperature

All ingoing and outgoing temperatures need to be known. If only a phase change occurs on one side, the temperature difference is taken as 1°C. CL-2079 is taken as an example, which cools down the bottom stream of the extractive distillation column to enter the solvent regeneration. The initial temperature is 245°C and it drops to 160°C. Cooling water is used to cool the stream. For every cooling

water stream, it is assumed to enter at 30°C and leave at 45°C. Cooling water then circulates between the heat exchanger and a cooling tower. When even further cooling is required, chilled water of 5°C can be used. For steam, the temperature depends on the pressure. Possible steam temperatures are listed in Table 49.[80]

Table 49: List of available steam utilities for heating purposes[80]

Steam	Pressure [psig]	Pressure [bar]	Temperature [°C]	Price [\$/ton]	$\Delta H_{\text{vap}}$ [kJ/kg]
Low	50	4.5	148	5.50	2119
Medium	150	11.4	186	8.80	1996
High	450	32.0	238	12.1	1770
Very high	595	42.0	254	19.0	1691

The temperatures for the example are given in Table 50.

Table 50: Stream temperatures for CL-2079

	Temperature (°C)	Description
$T_1$	245	Temperature of ingoing hot fluid
$T_2$	160	Temperature of outgoing hot fluid
$t_1$	30	Temperature of ingoing cold fluid
$t_2$	45	Temperature of outgoing cold fluid

The logarithmic temperature difference can then be calculated:[72]

$$\Delta T_{LM} = \frac{((T_1 - t_2) - (T_2 - t_1))}{\ln\left(\frac{T_1 - t_2}{T_2 - t_1}\right)} = 162.5^\circ\text{C} \quad (1.26)$$

Also the correction factor ( $F_T$ ) for the tube passes can be determined. This compensates for the partially co-current heat exchange in the tube passes. At first two factors, R and S, are determined. R is the ratio between flow rate times specific heat of shell and tube and S is a measure for the temperature efficiency.[72]

$$R = \frac{T_1 - T_2}{t_2 - t_1} = 5.67 \quad (1.27)$$

$$S = \frac{t_1 - t_2}{T_1 - t_1} = 0.07 \quad (1.28)$$

Then the correction factor is calculated with equation (1.29).[72]

$$F_T = \frac{(\sqrt{R^2 + 1} \ln\left(\frac{1 - S}{1 - RS}\right))}{(R - 1) \ln\left(\frac{(2 - S(R + 1 - \sqrt{R^2 + 1}))}{2 - S(R + 1 - \sqrt{R^2 + 1})}\right)} = 0.992 \quad (1.29)$$

#### 1.1.1.2. Required heat exchange area

The simulation gives a heat transfer of 455 kW and table 12.1 from [72] can be used to estimate an overall heat transfer coefficient (U). In the example, the cold fluid is water and the hot fluid is a mixture of DMC and phenol. This can be classified as organic solvent and therefore a heat transfer coefficient between 250 and 750 should be chosen. With  $U=300 \text{ W/m}^2\text{K}$ , the area can be calculated from equation (1.30).[72]

$$A = \frac{Q}{U\Delta T_{LM}F_T} = \frac{455 * 10^3}{300 * 162.5 * 0.992} = 9.41 \text{ m}^2 \quad (1.30)$$

The area is smaller than  $19 \text{ m}^2$ , therefore a double-pipe heat exchanger is used instead of a U-tube. Now the area has be recalculated, because there are no co-current flows and the correction factor becomes 1.[80]

$$A = \frac{Q}{U\Delta T_{LM}F_T} = \frac{455 * 10^3}{300 * 162.5 * 1} = 9.33 \text{ m}^2 \quad (1.31)$$

#### 1.1.1.3. Flow heating/cooling medium

With equation (1.32) the mass flow of either cooling water or steam can be calculated. In the example case there is no phase change of water, therefore the only the temperature difference in cooling water is responsible for the energy. [72]

$$m = \frac{Q}{c_p(t_2 - t_1)} = 7.26 \text{ kg/s} \quad (1.32)$$

Here the specific heat is calculated from the data sheet. In case of a heater, the temperature difference in this equation is  $(T_1 - T_2)$ .

#### 1.1.1.4. Other design parameters

There are some additional design parameters which need to be chosen: the material of shell and tube, tube length and pressure in the shell.

The usual material for both shell and tube is carbon steel, however sometimes operating conditions or fluid properties ask for another material of construction. In Table 51 a list of possible materials is provided. Also the price factor is included, this could be an issue in the decision making process. In equation (1.33), the material factor for the price can be calculated, the area is in square feet. [80]

$$F_M = a + \left(\frac{A}{100}\right)^b \quad (1.33)$$

Table 51: Materials for a shell and tube heat exchanger. Materials are indicated as Shell/Tube.[80]

<b>Material</b>	<b>a</b>	<b>b</b>
Carbon steel / Carbon steel	0	0
Carbon steel / Brass	1.08	0.05
Carbon steel / Stainless steel	1.75	0.13
Carbon steel / Monel	2.1	0.13
Carbon steel / Titanium	5.2	0.16
Carbon steel / Cr-Mo	1.55	0.05
Cr-Mo / Cr-Mo	1.7	0.07
Stainless steel / Stainless steel	2.7	0.07
Monel / Monel	3.3	0.06
Titanium / Titanium	9.6	0.06

Considering the tube length, there are some standard industrial sizes. Standard is a length of 20ft, but also 8, 12 or 16 ft can be chosen. However, deviating from the standard will cause an increase in heat exchanger costs. [80]

High pressure means a larger wall thickness and additional costs. Therefore, the operating pressure at the shell side is important for the economic evaluation.

In the example there are no extreme temperature of pressure conditions, however phenol is corrosive to carbon steel at high temperatures. So instead, stainless steel should be used in both shell and tube, as the phenol flows through the shell. The standard length of 20ft can be applied and the operating pressure at the shell side is 10 bar. [116]

#### 1.1.1.5. Summary

A summary of the equipment design of the heat exchanger is shown in Table 52.

Table 52: Summary of the design of CL-2079

<b>Required output</b>		
A	9.33E+00 m2	<i>Exchange area</i>
Type	Double-pipe	<i>Heat exchanger type</i>
Tube length	20 ft	<i>Length of tube</i>
Material	SS/SS	<i>shell/tube</i>
Pressure shell	10 bar	<i>Shell side pressure</i>
m_H2O	7.26 kg/s	<i>Cold medium flow</i>

Also for all other heaters and coolers, an equipment design is made. A summary of the output is given in Table 18.

Table 53: Summary of heat exchangers present in the process

Name	Type	Tin [C]	Tout [C]	Pshell [bar]	Duty [kW]	A [m <sup>2</sup> ]	Material [shell/tube]	Medium	Flow [kg/s]	Tube length [ft]
CL-2071	U-tube	120	20	30.0	-4.03E+03	6.48E+02	CS/CS	Chilled water	95.87	20
CL-20710	Double-pipe	89	20	1.0	-3.25E+01	4.72E+00	CS/CS	Cooling water	0.52	20
CL-2072	U-tube	52	20	1.0	-1.21E+03	1.84E+02	CS/CS	Chilled water	28.79	20
CL-2073	U-tube	137	85	10.0	-9.38E+02	2.23E+01	CS/CS	Cooling water	14.96	20
CL-2074a	Double-pipe	120	45	2.4	-7.77E+01	1.39E+01	CS/CS	Cooling water	1.24	20
CL-2074b	Double-pipe	122	60	5.0	-6.59E+01	8.81E+00	CS/CS	Cooling water	1.05	20
CL-2074c	U-tube	133	20	10.2	-2.76E+02	4.11E+01	CS/CS	Chilled water	6.57	20
CL-2075	U-tube	223	120	1.4	-3.42E+03	8.98E+01	CS/CS	Cooling water	54.55	20
CL-2076a	U-tube	128	40	3.0	-6.15E+02	1.79E+02	CS/CS	Cooling water	9.81	20
CL-2076b	U-tube	146	40	8.3	-7.55E+02	1.89E+02	CS/CS	Cooling water	12.04	20
CL-2076c	U-tube	144	95	23.5	-3.70E+02	3.11E+01	CS/CS	Cooling water	5.90	20
CL-2077	U-tube	124	65	0.7	-4.59E+02	2.99E+01	CS/CS	Cooling water	7.32	20
CL-2078	U-tube	95	20	1.2	-7.56E+02	1.62E+02	CS/CS	Cooling water	12.06	20
CL-2079	Double-pipe	245	160	10.0	-4.55E+02	9.33E+00	SS/SS	Cooling water	7.26	20
H-2071	U-tube	46	147	11.4	3.50E+03	2.97E+02	CS/CS	Steam medium	1.75	20
H-2072	U-tube	31	150	11.4	5.64E+03	9.29E+01	CS/CS	Steam medium	2.82	20
H-2073	U-tube	123	150	11.4	8.74E+02	2.44E+01	CS/CS	Steam medium	0.44	20
H-2074	U-tube	117	150	11.4	1.69E+03	4.49E+01	CS/CS	Steam medium	0.85	20
H-2075	Double-pipe	20	50	4.5	1.20E+02	1.43E+00	CS/CS	Steam low	0.06	20
H-2076	Double-pipe	21	125	4.5	4.10E+02	9.03E+00	CS/CS	Steam low	0.19	20
H-2078	U-tube	118	150	11.4	3.68E+03	9.85E+01	CS/CS	Steam medium	1.84	20
T-2071 Con	U-tube	51	50	0.3	-1.28E+03	1.87E+02	CS/CS	Cooling water	20.42	20
T-2071 Reb	U-tube	223	224	32.0	3.88E+03	1.68E+01	CS/CS	Steam high	2.19	20
T-2072 Con	U-tube	52	51	1.0	-6.50E+03	8.64E+02	CS/CS	Cooling water	103.68	20
T-2072 Reb	U-tube	95	96	4.5	2.13E+03	4.10E+01	CS/CS	Steam low	1.00	20
T-2073 Con	Double-pipe	137	136	10.0	-1.41E+03	1.68E+01	CS/CS	Cooling water	22.49	20
T-2073 Reb	U-tube	245	246	42.0	2.59E+03	3.27E+02	CS/SS	Steam very high	1.53	20
T-2074 Con	Double-pipe	89	88	1.0	-4.71E+02	1.09E+01	CS/CS	Cooling water	7.51	20
T-2074 Reb	Double-pipe	188	189	32.0	5.18E+02	1.06E+01	CS/SS	Steam high	0.29	20

For the economic analysis, the utilities are needed. In this case the utilities are the heating and cooling media. The total requirements for every utility is listed in Table 19.

Table 54: Total utilities needed for the heat exchangers

Utilities	
Chilled water	131.22 kg/s
Cooling water	280.83 kg/s
Steam low	1.25 kg/s
Steam medium	7.70 kg/s
Steam high	2.48 kg/s
Steam very high	1.53 kg/s

### I.1.2. Flash vessel

Gas-liquid separators are widely present in the process. Four of them are flash vessels, which are designed in this section. In general, there are two types of flash vessels; horizontal and vertical. Both require a different method of designing. At the end, a decision is made between horizontal or vertical, depending on the sizes of the vessels. For F-2071 an example calculation is given. The required input required is given in Table 55.

Table 55: Input for flash vessel design

Number	Gas flow [m <sup>3</sup> /s]	Liquid flow [m <sup>3</sup> /s]	Gas density [kg/m <sup>3</sup> ]	Liquid density [kg/m <sup>3</sup> ]
F-2071	0.618	3.59E-2	46.02	1067
F-2072	0.386	2.89E-3	65.64	1066
F-2073	0.761	1.53E-3	1.468	916.0
F-2074	0.048	2.17E-4	19.15	920.1

For the economic evaluation, the following parameters are needed and are returned from the calculations:[80]

- Vessel diameter [m]
- Vessel height [m]
- Operating temperature [°C]
- Operating pressure [bar]

#### 1.1.2.1. Settling velocity

Starting point for both a vertical and a horizontal flash vessel is the settling velocity of the liquid droplets. This is given in equation(1.34) and a result is given for the example.[72]

$$u_t = 0.07 \left( \frac{\rho_L - \rho_G}{\rho_G} \right)^{0.5} = 0.33 \text{ m/s} \quad (1.34)$$

This equation is valid if there is no demister pad used in the vessel, then  $u_s = u_t$ . If a demister pad is used, the settling velocity calculated in equation (1.34) should be multiplied by 0.15.[72]

#### 1.1.2.2. Demister pad

A demister pad is often used to improve the separating performance of a flash vessel. Especially when the droplets are very small. It actually increases the settling velocity. For the first calculations, let's assume there is no demister pad needed.[72]

In a vertical flash vessel, a demister pad reduces the diameter of the vessel. However, by reducing the diameter, the height of the vessel usually increases due to the required liquid hold-up. In principle for relatively low liquid flow rates a demister pad can be useful.

In a horizontal vessel, the residence time of gas and liquid are key parameters. A demister pad here reduces the vapour residence time required to settle the liquid droplets. So, only if the vapour residence time is limiting, a demister pad is useful to decrease the diameter and height of the vessel.

#### 1.1.2.3. Vertical vessel

In the first calculation it is assumed that there is no demister pad present. Therefore the settling velocity is now:

$$u_s = 0.15 * u_t = 0.05 \text{ m/s} \quad (1.35)$$

The diameter of the vessel can directly be calculated with the gas flow rate. This is done in equation (1.36).[72]

$$D = \sqrt{\frac{4\Phi_G}{\pi u_s}} = 3.99 \text{ m} \quad (1.36)$$

The height of the column depends on the diameter and the liquid hold-up. The liquid hold-up time is typically about 10 minutes and with the liquid flow rate the total volume of liquid inside the vessel can be determined:[72]

$$V_L = \Phi_L \tau_L = 21.54 \text{ m}^3 \quad (1.37)$$

With the diameter, the liquid height can easily be calculated.

$$h_v = \frac{V_L}{0.25\pi D^2} = 1.72 \text{ m}^3 \quad (1.38)$$

Also 0.15 m should be added for a level controller. Above and below the inlet there should be some space. Above the inlet this is equal to the diameter, but at least 1 m. Below the inlet it is equal to half the diameter, but at least 0.6 m. In the case of a demister pad, this needs space and typically 0.4 m is taken therefore. So the total height of the vessel can be determined with equation (1.39).[72]

$$H = h_v + h_{control} + h_{above} + h_{below} + h_{demister} = 7.86 \text{ m} \quad (1.39)$$

For this example, the use of demister pad is not favourable for the diameter to height ratio.

#### 1.1.2.4. Horizontal vessel

Also for the horizontal vessel, no demister pad is used at first. Here the diameter and height cannot be calculated separately. Some assumptions have to be made before a design can be made.

Three assumptions are needed. These are the length to diameter ratio, liquid height and fraction of the cross-section occupied by vapour ( $f_v$ ). For the length to diameter ratio, in general the operating pressure is used as a guide, see Table 56. Operating conditions in F-2071 are 30 bar and 120°C, so a length to diameter ratio of 4 is used.[72]

*Table 56: Length to diameter ratio*

Operating pressure [bar]	L/D
0-20	3
20-35	4
>35	5

If assumed that half of the vessel is occupied by liquid, then  $\frac{h_v}{D_v} = 0.5$  and  $f_v = 0.5$ .

Now, the actual and required residence time for the liquid and vapour need to be determined. First the vapour.

No demister pad is used, therefore the settling velocity is reduced as it was for the vertical vessel. For both actual and required residence time, the diameter of the vessel is needed. An iterative approach is chosen, where a vessel diameter is guessed and later on checked whether the actual residence time is longer than required.

The required residence time of the vapour to make sure the liquid droplets are settled at the liquid surface can be obtained with equation (1.40), with a diameter of 3 meter.

$$\tau_{vreq} = \frac{h_v}{u_s} = \frac{0.5D}{u_s} = 30.3 \text{ s} \quad (1.40)$$

The actual residence time is the length (obtained from length to diameter ratio) divided by the velocity of the gas.[72]

$$u_G = \frac{\Phi_G}{0.25\pi D^2 f_v} = 0.17 \text{ m/s} \quad (1.41)$$

$$\tau_{v_{act}} = \frac{L}{u_g} = \frac{4D}{u_G} = 68.6 \text{ s} \quad (1.42)$$

The liquid hold-up time is again 10 minutes at least. To determine the actual residence time, the volume of liquid inside reactor and the liquid flow have to be known. Equations (1.43) and (1.44) are used for the calculations.

$$V_L = L * 0.25\pi D^2(1 - f_v) = 42.4 \text{ m}^3 \quad (1.43)$$

$$\tau_{L_{act}} = \frac{V_L}{\Phi_L} = 1181 \text{ s} \quad (1.44)$$

For both the vapour and liquid, the actual residence time needs to be higher than required residence time. The diameter is the key parameter to change these and optimize the flash vessel. This is demonstrated in Table 57, where  $\Delta\tau_V$  and  $\Delta\tau_L$  should be minimal, but larger than 1. A diameter of 2.4 m and height of 9.6 m is optimal. This is limited by the liquid residence time and therefore a demister pad would not be of any help.

Table 57: Optimization of vessel diameter. ( $\Delta\tau_V = \tau_{v_{act}} - \tau_{v_{req}}$  and  $\Delta\tau_L = \tau_{L_{act}} - \tau_{L_{req}}$ )

<b>D [m]</b>	<b><math>\Delta\tau_V</math> [s]</b>	<b><math>\Delta\tau_L</math> [s]</b>
<b>4.0</b>	122.2	2200.3
<b>3.0</b>	38.3	581.4
<b>2.5</b>	14.44	83.67
<b>2.4</b>	10.87	4.87
<b>2.3</b>	7.67	-67.6

#### 1.1.2.5. Summary

For both vessels, the dimensions are known. The most compact one will be chosen for the final design. Table 58 shows that it is a difficult choice. At the end a vertical vessel is chosen for this separation, because it is a little bit more compact.

Table 58: Comparison of horizontal and vertical flash vessel

	<b>Horizontal</b>	<b>Vertical</b>
<b>D</b>	2.40	3.99
<b>L</b>	9.60	7.86

The other flash vessels are designed in a similar way and the results are given in Table 20.

Table 59: Summary of flash vessels in the process

<b>Name</b>	<b>Type</b>	<b>Po [bar]</b>	<b>To [°C]</b>	<b>Length [m]</b>	<b>Diameter [m]</b>	<b>Demister pad?</b>
<b>F-2071</b>	Vertical	30.00	120.00	7.86	3.99	N
<b>F-2072</b>	Vertical	29.80	20.00	3.79	1.34	Y
<b>F-2073</b>	Horizontal	0.80	20.00	3.00	1.00	Y
<b>F-2074</b>	Horizontal	10.00	20.00	1.80	0.60	N

### 1.1.3. Distillation column

Multiple distillation columns need to be designed for the process. A brief estimation of the height and diameter is carried out. These are the main parameters for the purchase cost. A total list is provided below:[80]

- Diameter [m]
- Length [m]
- Operating temperature [°C]
- Operating pressure [bar]

Then there are parameters which depend on the internals of the column. The first step in the design is to select the internal type; plates or packing. Depending on the internal the following parameters need to be known:[80]

- Number of trays (Plate)
- Type of tray (Plate)
- Material of tray (Plate)
- Structured or dumped packing (Packing)
- Length of packing (Packing)
- Number of distributors (Packing)

#### *1.1.3.1. Plates or packing*

So, the first decision to make is whether a column is filled packing or with trays. The book of Sinnott and Towler gives a list of advantages and disadvantages of both types[72]:

- Plate columns can handle a wider range of liquid and gas flow rates
- Packed columns are not suitable for very low liquid flow rates
- The prediction of the efficiency can be more accurate for a plate
- Plate columns can be designed with more assurance than packed columns
- Cooling coils can be placed on a plate
- In plate columns it is easier to withdrawal side streams
- Cleaning a plate column is more easy than packing, only with small diameter columns packing can be beneficial, than it can be replaced
- For corrosive liquids a packed column is usually cheaper
- Liquid hold-up is lower in a packed column. For safety reasons, this could be important
- Packed column are better to handle foaming mixtures
- Pressure drop per stage can be lower for packed column. For vacuum columns, packing should always be considered.
- Packing should always be considered for small-diameter columns (<0.6 m), then plates are difficult to install

For every column a decision is made between plate and packing according to these considerations. Distillation column T-2071 is a packed column. Operating pressure is below atmospheric pressure and therefore a packing is preferred. Other columns (T-2072, T-2073 and T-2074) are plate columns. All operate at atmospheric or elevated pressure and have significant liquid flows. The assurance of plate column is than preferred over a packing.

### 1.1.3.2. Plate column

Input for the columns are adapted from the UNISIM simulations. Density of the gas and liquid phase, the maximum gas flow rate and number of trays are needed for the calculations. The density of especially the gas phase varies long the column. Columns T-2072 and T-2073 have a vaporous distillate and a liquid bottom. The respectively gas and liquid densities inside the column are taken from these streams. The gas flow rate is calculated from the distillate stream and the reflux ratio (eq.(1.45)).

$$\Phi_G = D(1 + R) \quad (1.45)$$

Only the solvent regeneration column has a liquid outlet of the distillate. Here the column is temporary simulated with a gas outlet and the gas density is adapted from that. At every equilibrium stage the mass flow rate can be obtained. Then the volumetric flow rate can be determined. All parameters are given in Table 60.

Table 60: Input variables for the plate distillation columns

Number	Reflux ratio	Liquid density [kg/m <sup>3</sup> ]	Gas density [kg/m <sup>3</sup> ]	Distillate flow [m <sup>3</sup> /h]	Column gas flow [m <sup>3</sup> /s]	Number of trays
<b>T-2072</b>	3.28	986.9	1.697	5338	6.35	11
<b>T-2073</b>	1.84	821.4	10.59	294.5	0.232	24
<b>T-2074</b>	0.829	913.8	3.049	4818 [kg/h]	0.439	12

Another input parameter is the spacing between the trays. As first estimate a spacing of 0.5 m is taken. The spacing is normally between 0.15 and 1 m, depending on the operating conditions and column diameter. With the tray spacing, the maximum allowable gas velocity can be determined:[72]

$$u_v = (-0.171l_t^2 + 0.27l_t - 0.047) \left( \frac{\rho_L - \rho_v}{\rho_v} \right)^{0.5} \quad (1.46)$$

Now the diameter of the column can be calculated:[72]

$$D = \sqrt{\frac{4\Phi_G}{\pi u_v}} \quad (1.47)$$

The height of the column is determined by the number of trays. UNISIM simulation gives the theoretical number of equilibrium stages. The tray efficiency is needed to obtain the total number trays. A tray efficiency of 70% is used for the calculations. With the spacing between the trays and the 2 meter space at the top and bottom for liquid level and distributors the height of the column can be determined.[72]

### 1.1.3.3. Packing

In the process will be one column with packing, this is the distillation under decreased pressure. For this the same input is needed from the simulation (Table 61). The distillate is in the gas phase and the same method is used as for a plate column.

Table 61: Input data for a packed column

Number	Reflux ratio	Liquid density [kg/m <sup>3</sup> ]	Gas density [kg/m <sup>3</sup> ]	Distillate flow [m <sup>3</sup> /h]	Column gas flow [m <sup>3</sup> /s]	Number of trays
<b>T-2071</b>	0.216	1030	0.9038	56700	19.2	6

There are multiple options for the packing; dumped or structured. Structured packing operates under a lower pressure drop and has more theoretical stages per meter packing. A drawback are the increased costs of packing. For dumped packing a lot of options are available in terms of type, material and size. Table 62 gives an over view with the costs of the packing in dollar per cubic feet.

Table 62: Overview of dumped packings

Size	Installed costs (\$/ft <sup>3</sup> )				
	1 in.	1.5 in.	2 in.	3 in.	4 in.
Berl Saddles					
<i>Ceramic</i>	48	37	28		
Raschig rings					
<i>Carbon steel</i>	54	40	34	26	
<i>Stainless steel</i>	180	139	110	63	
<i>Ceramic</i>	26	21	19	15	
Intalox saddles					
<i>Ceramic</i>	34	28	24	19	
<i>Polypropylene</i>	37		23	12	
Pall rings					
<i>Carbon steel</i>	49	37	32		
<i>Stainless steel</i>	168	129	110		
<i>Polypropylene</i>	37	26	21	16	
Cascade mini-rings					
<i>Stainless steel</i>	134		95	70	52
<i>Ceramic</i>	90		70	56	
<i>Polypropylene</i>	90		70	56	
Tellerettes					
<i>Polyethylene</i>	76				

In the distillation column in the process, a structured packing is used. The type of packing is Mellapak 250.X from Sulzer. Designing such a packing needs information distributed by the vendor. Figure 117 is provided from Sulzer. A capacity factor is the parameter which determines the diameter of the column.[81]

$$F = \frac{\Phi_G}{0.25\pi D^2} \sqrt{\rho_G} \quad (1.48)$$

The optimal operating range is in the horizontal part of the graph, there a small change in feed does not have a major effect on the separation performance. Therefore, a factor of 2 is chosen. According to the graph, 2.1 theoretical equilibrium stages are present in one meter packing. With that knowledge the height of the column is determined, also here a 2 meter space at the top and the bottom is taken. To distribute the liquid, a distributor is needed. There are two places where liquid enters the column, the reflux at the top and the feed, so two distributors are needed.

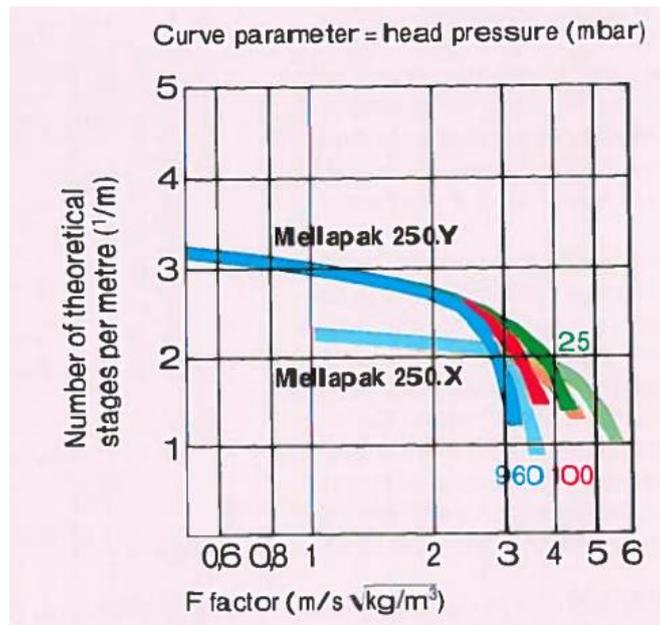


Figure 117: Performance of Mellapak 250.X provided by the supplier

#### 1.1.3.4. Summary

A summary of the design of all distillation columns is given in Table 21. In total four columns are installed of which one is packed column and the other three are plate columns. The design confirms the statement made in chapter 6 that the extractive distillation and solvent regeneration are smaller. Although the extractive distillation column is relatively high, the diameter is small.

Table 63: Overview of distillation columns present in the process

Number	Internal	Diameter [m]	Height [m]	To [°C]	Po [bar]	NT	Type	Material	Packing	Packing	
										Packing length [m]	# Distributors
T-2071	Packing	3.41	6.86	223.2	0.5	-	-	-	Structured	2.86	2
T-2072	Plate	2.72	12.00	95.5	1.2	16	Sieve	CS	-	-	-
T-2703	Plate	0.86	21.50	224.9	10.2	35	Sieve	SS316	-	-	-
T-2074	Plate	0.85	13.00	187.7	1.2	18	Sieve	SS316	-	-	-

#### 1.1.4. Pump

Pumps are used to pump liquid stream to a desired pressure. In the process a total of nine pumps are operating. Every pump is designed. Primarily the design consists of selecting a suitable pump type for the operation.

Available pumps are a centrifugal pump, gear pump or reciprocating plunger pump. Centrifugal pumps are most widely purchased and the cheapest of them all. However, a gear pump and reciprocating plunger pump are able to operate under a more wide range of flow rates and pump heads. Especially for a plunger pump, as the pump is larger, the costs increase rapidly. Therefore even two centrifugal pumps in series or parallel would be cheaper than one plunger pump. For each pump the required output is discussed.[80]

1.1.4.1. Electric motor

The pumps need and electric motor to drive them. Usually the costs of the motor are not included in the correlations for the pumps. For the costs only the power consumption is needed. This can be calculated from equation (1.55).[80]

$$P_C = \frac{P_B}{\eta_M} = \frac{QH\rho}{33,000\eta_P\eta_M} \tag{1.49}$$

The pump efficiency depends on the pump type and will be discussed in the concerned sections. For the motor efficiency an estimation is given in equation (1.56).[80]

$$\eta_M = 0.80 + 0.0319 \ln P_B - 0.00182(\ln P_B)^2 \tag{1.50}$$

A minimum of one horsepower is needed for the motor. If the calculations conclude that less power is needed, the minimum of one is be used for the economics.

The head has three aspects; static head, pressure head and velocity head. Static head can only be determined as the lay-out of the plant is known, as this is not the case, it is assume that all equipment is at the same level. Also no information is present about the velocity of the streams, this is usually not of importance, so it is neglected. Then only the pressure head remains and can be determined with:[80]

$$H = \frac{P_{out} - P_{in}}{\rho g} \tag{1.51}$$

These assumptions are valid for a high pressure difference.

1.1.4.2. Choosing a pump

There are three types of pumps to choose from and all have little different operating ranges. When the possible pump types applicable in the operating ranges, a decision can be made based on the price.

The centrifugal pump can handle a wide range of flow rates and heads. Table 64 gives the possibilities and the price factor of the different options.[80]

Table 64: Possible centrifugal pumps and their operating ranges[80]

Type	No. of stages	Shaft rpm	Case-split orientation	Flow min (gpm)	Flow max (gpm)	Head min (ft)	Head max (ft)	Maximum motor Hp	Price factor
A	1	3600	VSC	50	900	50	400	75	1.0
B	1	1800	VSC	50	3500	50	200	200	1.5
C	1	3600	HSC	100	1500	100	450	150	1.7
D	1	1800	HSC	250	5000	50	500	250	2.0
E	2	3600	HSC	50	1100	300	1100	250	2.7
F	2+	3600	HSC	100	1500	650	3200	1450	8.9

A gear pump can be applied for a flow rate between 10 and 900 gallons per minute and the maximum pressure at the outlet is about 13 bar.[80]

The last option is a reciprocating plunger pump. It has the widest operation range in terms of flow rate and head of the three options. In this case the important parameter is the brake horsepower. If it is between 1 and 200, a reciprocating plunger pump is suitable for the operation.[80]

If there is no pump suitable for the given flow rate and head, there are some options. If the head is too high, two (or more) pumps can be placed in series, both generate one part of the head. When the flow is too high for the pumps, two (or more) can be operated in parallel, with each handling a part of the total flow.

Then there is the possibility that the head and/or the flow is too low. Then a plunger pump is chosen as best option, because this has the lowest operating possibility.

#### *1.1.4.3. Pump efficiency*

The efficiency of the pump is different for each type. Equations give the pump efficiency for a centrifugal pump, where the flow rate is in gallons per minute.[80]

$$\eta_p = -0.316 + 0.24015 \ln Q - 0.01199(\ln Q)^2 \quad (1.52)$$

For a gear pump the efficiency depends on the kinematic viscosity, where the kinematic viscosity is given in centistokes:[80]

$$\begin{aligned} \nu < 20 &\rightarrow \eta_p = 0.8 \\ \nu < 500 &\rightarrow \eta_p = 0.5 \end{aligned} \quad (1.53)$$

A reciprocating plunger pump, always has an efficiency of 0.9.

#### *1.1.4.4. Material*

At last, the material type is chosen. The standard material is cast iron or carbon steel, only for corrosive compounds, high temperatures or other special occasions a different material is used. For a centrifugal pump and gear pump the list is:[80]

- Cast iron
- Ductile iron
- Cast steel
- Bronze
- Stainless steel
- Hastelloy C
- Monel
- Nickel
- Titanium

For a reciprocating plunger pump, the list is a little shorter:[80]

- Ductile iron
- Ni-Al-Bronze
- Carbon steel
- Stainless steel

#### 1.1.4.5. Summary

A summary of the pumps is given in Table 22. In total there will be five reciprocating plunger pumps, three gear pumps and one centrifugal pump. A centrifugal pump is indicated with a letter corresponding to Table 64.

Table 65: Summary of the pumps present in the process

Number	Flow rate	Head	Pump	Power	$\eta_P$	$\eta_M$	Material
	[m <sup>3</sup> /s]	[m]	type	[Hp]			
<b>P-2071</b>	1.42E-02	378.70	Plunger	68.57	0.90	0.90	Carbon steel
<b>P-2072</b>	1.35E-05	277.40	Plunger	1.25	0.90	0.80	Carbon steel
<b>P-2073</b>	1.53E-03	106.83	Plunger	2.66	0.90	0.82	Carbon steel
<b>P-2074</b>	1.19E-03	286.16	Plunger	4.31	0.90	0.84	Carbon steel
<b>P-2075</b>	6.88E-04	1.92	Gear	1.00	0.80	0.65	Cast iron
<b>P-2077</b>	2.11E-02	300.18	E	133.40	0.67	0.91	Cast iron
<b>P-2078</b>	2.33E-02	8.88	Gear	4.20	0.80	0.84	Cast iron
<b>P-2079</b>	2.17E-04	4.43	Plunger	1.25	0.90	0.80	Carbon steel
<b>P-20710</b>	1.89E-03	100.40	Gear	3.43	0.80	0.83	SS

#### 1.1.5. Compressor

Compressors are needed to compress gas streams to a desired pressure. In the process some high pressure unit operations are present and gaseous compounds as CO<sub>2</sub> are present in the system. In total five compressors are needed in the process. All are designed in this section. The output needed for the economics are:

- Compressor type
- Gas flow rate [m<sup>3</sup>/s]
- Ingoing pressure [bar]
- Outgoing pressure [bar]
- Power consumption [Hp]
- Material
- Motor type

The compression ratio defines the type of compressor. For a compression ratio of less than two the compressor can be classified as blower and this will reduce the costs significantly. An example is given for both options. The input data obtain from the UNISIM simulation is shown in the following table:

Table 66: Input data for the compressors

Number	Pin [bar]	Pout [bar]	Specific heat ratio	Inlet flow rate [m <sup>3</sup> /s]
<b>CP-2071</b>	1.0	30.2	1.282	4.28
<b>CP-2072</b>	29.8	30.2	1.547	0.386
<b>CP-2073</b>	0.3	1.2	1.395	15.8
<b>CP-2074</b>	0.8	10.2	1.288	0.761
<b>CP-2075</b>	10.0	30.2	1.340	0.048

### 1.1.5.1. Blower

For compression ratios below 2, a compressor is classified as blower. Therefore, a slightly different design calculation is needed. In the next section, a blower is designed. One blower is suitable for this, CP-2072. This is the CO<sub>2</sub> recycle stream where only a small pressure drop has to be overcome.[80]

Two types of blowers are generally available, a centrifugal blower and rotary straight-lobe blower. Operating conditions and efficiency are given in Table 67. A centrifugal blower is cheaper than a rotary straight-lobe.[80]

Table 67: Overview of blower types

Blower type	Minimum flow rate [ft <sup>3</sup> /min]	Maximum flow rate [ft <sup>3</sup> /min]	Efficiency [%]
Centrifugal	100	50,000	70-80
Straight-lobe	20	50,000	50-70

With the input data, the power consumption can be calculated from following set of equations. A centrifugal blower is used with an efficiency of 75%.[80]

$$P_B = 0.00436 \left( \frac{k}{k-1} \right) \frac{Q_I P_I}{\eta_B} \left( \left( \frac{P_O}{P_I} \right)^{\frac{k-1}{k}} - 1 \right) = 27.5 \text{ Hp} \quad (1.54)$$

$$P_C = \frac{P_B}{\eta_M} = 31.0 \text{ Hp} \quad (1.55)$$

$$\eta_M = 0.8 + 0.0319(\ln P_B) - 0.00182(\ln P_B)^2 = 0.89 \quad (1.56)$$

Only the material of construction has to be chosen. Here the choice is between cast iron, stainless steel, fiberglass, nickel alloy or aluminium. As there are no corrosive materials or other limitations, a cast iron blower is selected. The motor type is included in the price calculations for a blower.[80]

### 1.1.5.2. Compressor

Compression ratios above two require a compressor. In this section the compressor for the CO<sub>2</sub> feed is designed as example. In most cases multistage compressors are needed with interstage cooling. In the flowsheet these are separately included, however for the purchase costs these are combined in one unit. For the interstage cooling, the heat exchangers are designed in section I.1.1.

Three compressor types are available with different capacity, pressure range and efficiency. These are given in Table 68.[80]

Table 68: Overview of possible compressors

Type	Q <sub>min</sub> [ft <sup>3</sup> /min]	Q <sub>max</sub> [ft <sup>3</sup> /min]	P <sub>max</sub> [psig]	Max Hp	Efficiency [%]
Centrifugal	1,000	150,000	5,000	30,000	70-75
Reciprocating	5	7,000	100,000	20,000	80-90
Screw	800	20,000	400	6,000	75-85

The CO<sub>2</sub> feed has a flow rate of 9070 gpm, a pressure output of 440 psig and a power consumption of 4085 Hp. From these parameters only the centrifugal compressor is able to handle the CO<sub>2</sub> stream. With an efficiency of 75%, the brake horsepower can be calculated from equation (1.54). A compressor does not always need an electric motor. Also a steam turbine or gas turbine are suitable, however the efficiency is much lower, 65% and 35% respectively, compared to a electric motor, 95%. The needed brake horsepower is 3880 Hp and including the motor efficiency the power consumption is than 4084 Hp. No special compounds are present, therefore the material of the compressor is carbon steel.

### 1.1.5.3. Summary

Similar calculations are carried out for the other compressors and the results are summarized in Table 24. Three centrifugal compressors and one reciprocating compressor are selected.

Table 69: Summary of the compressors in the process

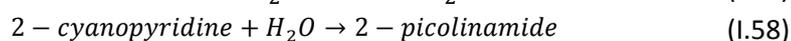
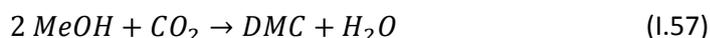
Number	Type		Gas flow [m <sup>3</sup> /s]	Pin [bar]	Pout [bar]	Power [Hp]	Material	Motor
CP-2071	Compressor	Centrifugal	4.28	1.00	30.20	4084.20	Carbon steel	Electric
CP-2072	Blower	Centrifugal	0.39	29.80	30.20	31.01	Cast iron	-
CP-2073	Compressor	Centrifugal	15.80	0.30	1.20	1513.36	Carbon steel	Electric
CP-2074	Compressor	Centrifugal	0.76	0.80	10.20	392.63	Carbon steel	Electric
CP-2075	Compressor	Reciprocating	0.05	10.00	30.20	101.40	Carbon steel	Electric

### 1.1.6. Reactor design

In this chapter a detailed model of the reactor is constructed. The reactor that is modelled is R-2071.

#### 1.1.6.1. Reaction

There are two reactions happening in the reactor. The first reaction, (I.57), is the conversion of methanol and CO<sub>2</sub> into DMC and water. The equilibrium is unfavourable towards the product side. Therefore, a dehydrating agent is added to the reaction mixture to remove the water and thus shift the equilibrium. The second reaction, (I.58), is the reaction of the agent with water. This set up is discussed by Bansode et al. and Honda et al. [6, 7]. CeO<sub>2</sub> is used as a catalyst, it catalyses both reactions. It is assumed to be first order in CO<sub>2</sub> because of the big surplus of methanol at the catalyst surface.



#### 1.1.6.2. Kinetics

The kinetics were hard to estimate because of the little information available, a fit was made on the data available of Honda, but this showed third order reaction kinetics for a single component [6]. Since this was very unlikely with the low CO<sub>2</sub> concentration it was finally decided to assume a first order reaction because of the high methanol concentration compared to the CO<sub>2</sub> concentration. Bansode et al. stated that the production of DMC was 1 g/g<sub>cat</sub>h [7]. From this and the assumption of a first order reaction the kinetic constant can be calculated. The concentration of CO<sub>2</sub> at steady state operation was 360 mol/m<sup>3</sup>. The resulting k in 1/s is then:

$$\frac{1 * \rho_{cat}}{C_{CO_2} * m_{DMC} * 3600} = \frac{1 * 5300000}{360 * 90.08 * 3600} = 0.0045 \text{ s}^{-1} \quad (\text{I.59})$$

This is at a temperature of 120°C, the reaction rate is assumed to double with an increase in temperature of 10°C because other temperature dependency is not available, thus this rule of thumb is used.

The reaction rate constant for the dehydration reaction is assumed to be 10 m<sup>3</sup>/mol \* s for a second order reaction in 2-cyanopyridine and water concentration. This value is not based on any data however. It is there to show that the dehydration gets the equilibrium reaction to go to the products side, the reaction is not rate limiting and thus this value is a good representation of the system.

### 1.1.6.3. Operating conditions/reactor choice

Bansode et al. obtained good results with respect to conversion and selectivity for a range of pressures (over 30 bar), but only for a temperature of 120°C, otherwise the reaction was very slow (lower temperatures) or side products started forming (higher temperatures) [7]. If the pressure is 30 bar, maximum conversion is reached. The rate of formation of side products increases dramatically when the temperature reaches over 130°C. From this it can be concluded that the temperature inside the reactor should stay under 130°C and would preferably be operated at a pressure of 30 bar. The compounds and their state under the preferred conditions are displayed in Table 70.

Table 70: Compounds in the reactor and their state

Compound	State (30bar, 120°C)
Methanol	L
CO <sub>2</sub>	G
DMC	L
Water	L
2-Cyanopyridine	L
2-Picolinamide	L
CeO <sub>2</sub>	S

The three phases result in little choices for the type of reactor, a slurry reactor or a trickle bed can be chosen. Other alternatives are exotic like a fixed bed bubble column or a three phase fluidized bed [117]. The volume fraction of the gas phase in the reactor is much higher than the liquid phase. This is because of the higher general volume of gasses, but also due to an excess of the CO<sub>2</sub> in the system. This leads to a system in which the liquid flows over the solids catalyst and the gas flows in between these states; a trickle flow reactor. The reactor has a relatively high adiabatic temperature rise ( $T_{ad} = 232^{\circ}\text{C}$ ) and a small temperature operating range. Thus a multitubular reactor is needed.

### 1.1.6.4. Operation

It is probably beneficial to run the reactor in a counter current operation due to the reaction being an equilibrium reaction; therefore the conversion is higher when the concentration differences are as big as possible, because the higher product concentrations combined with higher reactant concentrations would maintain the equilibrium. If the concentration of CO<sub>2</sub> in the reactor is highest at the outlet of the products the equilibrium is less likely to shift to the reactant side. However, the carbon dioxide concentration in the liquid is nearly uniform over the reactor length as can be seen in Figure 121 so co-current operation is chosen because it is easier to operate.

The adiabatic temperature rise in the reactor is relatively high, around 232°C. As a result, a system with multiple tubes with outside cooling is needed.

### 1.1.6.5. Correlations

A variety of correlations were used to estimate the mass transfer and heat transfer coefficients in the system. Except for these a lot of fits were made from the data points found on the NIST professional web book to estimate the temperature dependency of the enthalpy of formation, viscosity, thermal conductivity, specific heat capacity and density of all components.

#### I.1.6.5.1. Mass transfer coefficients

The mass transfer coefficients were calculated using Sherwood correlations from Krishna and Wesselingh, this correlation is valid for a counter-current trickle bed system, it is assumed that it also fits for co-current systems [118]. There is no mass transfer resistance in the gas phase, because it is pure CO<sub>2</sub>. Thus, all the resistance is in the liquid phase. The correlation used to estimate this mass transfer resistance is [118]:

$$Sh = 19 * Re(L)^{\frac{1}{2}} * Sc(L)^{\frac{1}{3}} \quad (I.60)$$

This results in the following mass transfer coefficient:

$$k_L = Sh * \frac{D}{d_p} \quad (I.61)$$

In which  $d_p$  is the particle diameter of the catalyst species. This mass transfer coefficient was used to describe the transfer in the gas liquid interface and the liquid solid interface. This was possible because of the lack of mass transfer resistance in the gas phase with a pure stream.

#### I.1.6.5.2. Heat transfer coefficients

The transfer of heat from the system through the outside wall and to the cooling water is also described by correlations. The overall heat transfer coefficient  $\alpha$  can be estimated by the following equation [72]:

$$\frac{1}{\alpha} = \frac{d_{to}}{d_{ti}} * \frac{1}{\alpha_{water}} + \frac{d_{to}}{d_{ti}} * \frac{1}{w_{ff}} + \frac{2 * k_{steel}}{d_{to} * \ln\left(\frac{d_{to}}{d_{ti}}\right)} + \frac{1}{\alpha_{tubeside}} + \frac{1}{f_{ft}} \quad (I.62)$$

In this equation the following abbreviations were used:

Table 71: Abbreviations used

Abbreviation	Meaning
<b>dto</b>	Outside tube diameter
<b>dti</b>	Inside tube diameter
<b>wff</b>	water fouling factor
<b>fft</b>	Tube side fouling factor

The thickness of the tube wall used was 5 mm. This value was chosen to ensure the mechanic strength of the system. The  $\alpha$  on the water side and the  $\alpha$  on the tube side are estimated. The following correlations were used for this:

$$Nu_{tube} = Re_{gas}^{0.8} * Pr_{gas}^{0.33} \quad (I.63)$$

While the shell side Nusselt number is defined by [72]:

$$Nu_{shell} = j_h * Re_{shell} * Pr_{shell}^{0.33} \quad (I.64)$$

In which  $j_h$  is the heat transfer coefficient, which depends on Reynolds and the baffle cut off in the shell. For the overall heat transfer coefficient it was assumed that only the gas phase was in contact with the tube wall.

The fouling factors are estimated at 3000 m<sup>2</sup>\*°C\*W<sup>-1</sup> for the shell side for river water and 5000 m<sup>2</sup>\*°C\*W<sup>-1</sup> for the tube side for organic vapours, these are general values to take for this [72].

#### 1.1.6.5.3. Solubility CO<sub>2</sub> in methanol

The solubility of CO<sub>2</sub> in methanol was estimated with Henry's law [119]:

$$\ln\left(\frac{f}{x}\right) = \ln(H) + \frac{(V^\infty * P_{CO_2})}{R * T} \quad (1.65)$$

In this equation f is the concentration of CO<sub>2</sub> in the liquid phase, x the concentration of methanol, V<sup>∞</sup> is the molar volume of CO<sub>2</sub> in methanol and H is the Henry constant of CO<sub>2</sub>.

#### 1.1.6.5.4. Estimation of diffusion coefficients

The diffusion coefficients in the medium were estimated by calculating the pure compound diffusion coefficients of the compounds in pure 2-cyanopyridine and methanol. These values were then averaged to find the diffusion coefficients, these diffusion coefficients are all in the same phase, so they are all in the same order of magnitude. The pure compound coefficients were estimated using the Wilke-Chang equation:

$$D = 7.4 * 10^{-8} * \sqrt{\frac{T * M_{solvent}^{0.5}}{V_{solute}^{0.6} * \eta_{solvent}}} \quad (1.66)$$

In this equation the T is the assimilation factor. This represents the strength between the bonds in the solvent. For methanol this factor is 1.9 and for 2-cyanopyridine it is 1. M represents the molar mass of the solvent, V is the molecular volume of the diffusing species and η is the dynamic viscosity of the solvent.

#### 1.1.6.6. Equations used for modelling

The reactor is modelled by making balances over the gas and liquid phase, with concentrations in the gas phase, liquid bulk and catalyst surface. This is done by using a PFR model with decreasing superficial velocity for the gas and with decreasing concentrations for the liquid phase. The density, viscosity, diffusivity, reaction rate and equilibrium are a function of temperature and are modelled as such.

The reactor was modelled by putting multiple PFR models in contact with each other. The gas phase was described by the following equation, it involves the slowdown because of diffusion of the CO<sub>2</sub> to the liquid phase:

$$\frac{du}{dx} = -a * kLCO_2 * \frac{m * C_{CO_2gas} - C_{CO_2liquid}}{C_{CO_2gas}} \quad (1.67)$$

In this kLCO<sub>2</sub> is the mass transfer coefficient, a the specific surface area of the catalyst (m<sup>2</sup>/m<sup>3</sup>). m is the compensation factor for the solubility in methanol of CO<sub>2</sub>, it is a factor that describes the ratio between the CO<sub>2</sub> concentration in the gas and the CO<sub>2</sub> concentration in the liquid.

The liquid phase balance for CO<sub>2</sub> is defined as the following:

$$ul * \frac{dC}{dx} = a * kLCO_2 * (m * C_{CO_2gas} - C_{CO_2liquid}) - a * kLCO_2 * (C_{CO_2liquid} - C_{CO_2solid}) \quad (1.68)$$

The other balances do not have the incoming species, thus only the second part of the equation is present there:

$$u_l * \frac{dC}{dx} = -a * kLCO_2 * (C_{liquid} - C_{solid}) \quad (1.69)$$

The equation that describes the diffusion of the species from the liquid phase to the solid interface is described by:

$$a * kL * (C_{liquid} - C_{solid}) = k * C_{sCO_2} - \frac{k}{K_{eq}} * C_{sH_2O} * C_{sDMC} \quad (1.70)$$

The right side of this equation is times two for methanol due to stoichiometry. The right side of this equation is now defined as R1 in further equations.

For water an extra reaction term is added to describe the reaction from the dehydration reaction:

$$a * kL_{water} * (C_{solid} - C_{liquid}) = k * C_{sCO_2} - \frac{k}{K_{eq}} * C_{sH_2O} * C_{sDMC} - k_2 * C_{H_2O} * C_{pyr} \quad (1.71)$$

The balance with DMC is similar without the dehydration reaction part.

The heat generated and removed from the reactor is determined by the speed at which the medium inside the reactor is flowing, the reaction rate, cooling temperature and the surface area through which the heat is removed from the reactor:

$$\frac{dT}{dx} = \frac{r_{tot} * dH_{reaction} - \alpha_{total} * \frac{4}{d_{tube}} * (T - T_c)}{Cp_l * u_l * c_l + Cp_g * u_g * c_g} \quad (1.72)$$

#### 1.1.6.7. The catalyst

The catalyst is a cerium oxide without a carrier. The cerium oxide that was used for the design of this reactor is for sale at Sigma-Aldrich [120]. It has the following properties:

Table 72: Catalyst properties

Parameter	Value
Specific surface area	30 m <sup>2</sup> /g
Catalyst bulk density	7650 kg/m <sup>3</sup>
Surface area per cubic meter	56 m <sup>2</sup> /m <sup>3</sup>

This catalyst has be replaced every month because of rapid catalyst deactivation [6]. Therefore, additional reactor shells are needed to replace the catalyst, but still be able to produce.

#### 1.1.6.8. Starting point for the reactor

To optimise the reactor certain goals are defined, these are given in Table 73.

Table 73: Reactor design constrains

Parameter	Value
Reactor temperature	<130°C
C <sub>methanol</sub> /C <sub>2-cyanopyridine</sub>	2
Mol CO <sub>2</sub> in/mol methanol in	2.5
DMC production	450 kton/year
Methanol Conversion	>92.4%
Gas velocity	<0.6 m/s
Liquid mass velocity	<12 kg/m <sup>2</sup> /s

The demand for the gas velocity is to ensure that the reactor stays in the trickle flow regime. Otherwise catalyst wetting will not be ideal. The temperature constraint is because of side product formation. The conversion and methanol/CO<sub>2</sub> ratio are what Bansode reached and used. It is attempted to reach these same conditions. The production constraint comes from the scope, the goal is to make this amount of DMC to produce enough to use it as a fuel additive.

The parameters that can be varied to achieve these constraints are:

- Reactor length
- Amount of reactor tubes
- Reactor tube diameter
- Inlet temperature
- Cooling temperature
- Catalyst particle diameter
- The gas velocity can be lowered, with the liquid velocity in equal amounts

The reactor will be in a configuration with multiple tubes. The shell in which these tubes are put in is set to have a maximum diameter of 1.52m for practical reasons [72].

#### 1.1.6.9. The optimization process

All the previously mentioned parameters were varied to find a variety of configurations in which the goal parameters were met. The inlet and cooling temperature were kept at 120°C because the lower temperatures lead to much lower kinetics and thus much bigger reactors. This resulted in the following configurations:

Table 74: Reactor options  $P_{in}=3*10^6$  Pa,  $T_{in}=120^{\circ}\text{C}$

	$u_{in}$ [m/s]	$d_t$ [m]	$L$ [m]	# of tubes	$d_p$ [m]	$T_{max}$ [°C]	Conversion	Production (kton/year)	# shells
#1	0.1	0.04	8	8000	0.005	128.7	94.6	452	16
#2	0.2	0.065	14.5	1575	0.005	129.6	92.7	461	8
#3	0.2	0.06	16	1750	0.005	128.0	93.6	448	8
#4	0.2	0.06	17	1820	0.003	127.2	92.7	454	8
#5	0.3	0.08	22	688	0.005	129.8	93.5	461	6
#6	0.5	0.1	37.5	260	0.005	128.8	92.8	451	3
#7	0.5	0.02	57.5	6525	0.005	121.1	92.8	452	4

These iteration processes were started by changing the superficial gas velocity. This gas velocity is connected to the liquid superficial velocity to ensure that the composition going into the reaction is as specified. The tube diameter was then varied to make sure the temperature in the reactor did not become too high. The tube length was changed after that to make sure the right conversion was met after which the amount of tubes was varied to reach the right capacity. The length and amount of tubes have an effect on the temperature in the tube. However, this effect is minor compared to the tube diameter.

Option 2 has the optimum configuration for tube diameter, length, amount of tubes and gas velocity. So this is the configuration chosen. The tubes need to stand upright, because gravity is used to let the liquid flow over the catalyst. When the amount of tubes is made less, the reactor length becomes significantly larger, a vessel that is too high would lead to trouble with accessibility and the wind. A lot of small tubes will result in a high pressure drop, which is unwanted, also more material would be needed to get the same results. If the gas velocity is too high the reactor will become too long, while a too low velocity results in very small tube diameters because the heat is not handled properly. The cooling water which is used must be at 120C, therefore it must be pressurized to 3bar.

#### 1.1.6.10. Reactor overview:

Option #2 as seen in Table 74 was chosen because of its optimum between tube diameter, length and amount of tubes. The conversion at the end is 92.8%, the conversion at different stages in the reactor is shown in Figure 118. The concentration of DMC and water are shown in Figure 119, concentrations on the catalyst surface and in the liquid bulk are similar because the system is reaction rate limited.

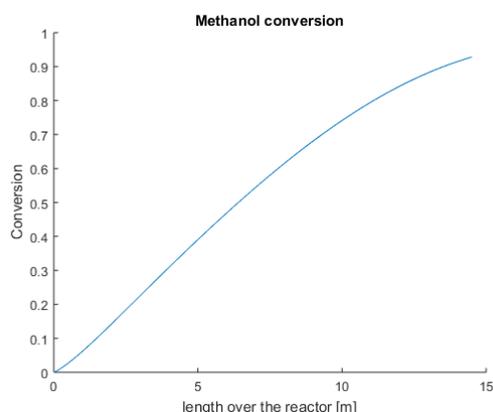


Figure 118: Methanol conversion over the reactor

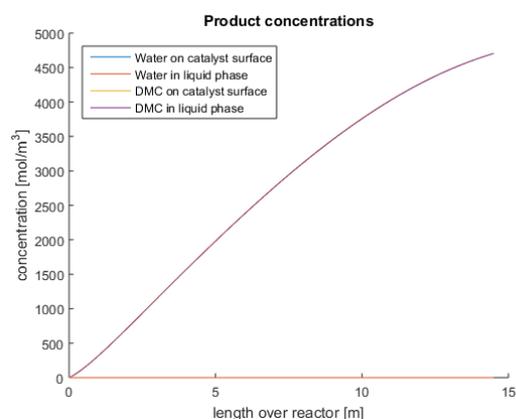


Figure 119: Reaction product concentrations

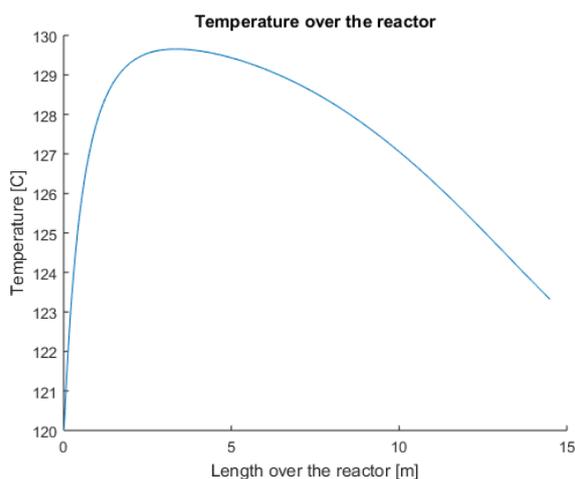


Figure 120: Temperature profile over the reactor

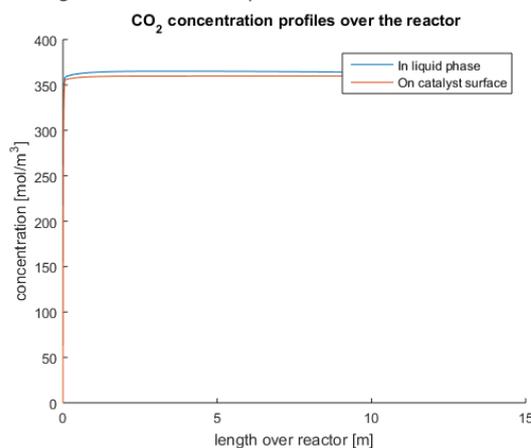


Figure 121: CO<sub>2</sub> concentrations over the reactor in liquid and gas phase

The temperature initially increases because the heat produced by the reactions is more than the heat removed through the tube wall. However, this changes later because of the lowering dehydration reaction rate because of the lower 2-cyanopyridine concentration. That is why from that point the temperature slowly decreases over the reactor as can be seen in Figure 120.

### 1.1.6.11. Reactor checks

Some checks were put on the reactor to ensure that the model was right. This includes checks if axial and radial dispersion are negligible and if the reactor is in trickle flow regime.

Axial dispersion is negligible if the following statement is true [121]:

$$0.05 > \left| \frac{n * Da_I}{Pe_m} - \frac{Ar * Da_{III}}{Pe_h} \right| \quad (1.73)$$

In this equation the n is for the reaction order and Ar is the activation energy of the reaction divided by the gas constant and the temperature in Kelvin. This energy is not known in literature and is therefore the Ar factor is estimated to be 1000. The other factors are dimensionless numbers that are defined by:

$$Da_I = \frac{(r_{eff} * d_p)}{U_s * C_0} \quad (1.74)$$

$$Da_{III} = - \frac{\Delta H_r * r_{eff}}{\rho_g * U_s * T_w * C_p} \quad (1.75)$$

$$Pe_m = \frac{U_s * d_p}{D} \quad (1.76)$$

$$Pe_h = \frac{\rho_g * u_s * d_p * u_s}{\lambda} \quad (1.77)$$

For this configuration this statement is true with a maximum value of  $6 * 10^{-4}$  for this value.

The check if radial dispersion is negligible in the reactor is defined by [121]:

$$\left| \frac{-\Delta H_r * r_{eff} * d_t^2}{\lambda_r * T_w} \right| * Ar - \frac{1.6}{1 + \frac{8}{Bi}} < 0 \quad (1.78)$$

In this case the dimensionless Biot number is defined by:

$$Bi = \frac{\alpha_w * d_t}{\lambda_{eff}} \quad (1.79)$$

The  $\lambda_r$  is the thermal dispersion coefficient in the reactor system which is defined by [121] :

$$\lambda_r = \frac{dp * \rho_{species} * Cp_{species} * ul}{Pe} \quad (1.80)$$

The Peclet number for the reactor is estimated to be 8 [121].

In this case the effect of radial dispersion is calculated for the liquid phase because this is the phase where the least turbulence will happen and thus the least amount of mixing. The resulting maximum value is -1.58 and thus it can be assumed that radial dispersion can be neglected.

The trickle flow regime is defined by Krishna and Sie for an air-water system [122]. Since there is no information for our specific system it is assumed that this also applies to a CO<sub>2</sub>-methanol-DMC system. The regimes are shown in Figure 122 and Figure 123.

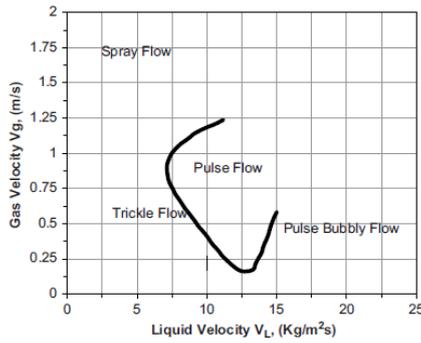


FIGURE 2 Flow regime map (Sic & Krishna, 1998).

Figure 122: Mass transfer regimes in multiphase reactors

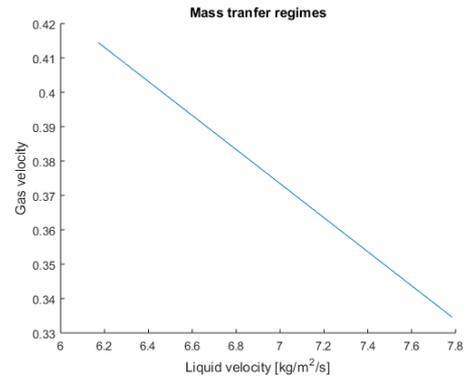


Figure 123: Regimes in the reactor modelled.

The mass transfer changes from the high gas velocity in the beginning of the reactor to the higher liquid velocity in the end of the reactor because of the CO<sub>2</sub> continuous dissolving. Comparing Figure 122 to Figure 123 shows that trickle flow is present in the reactor.

#### 1.1.6.12. Pressure drop over the reactor

The pressure drop was calculated using an equation experimentally derived from the Ergun equation by Wammes and Westerterp:

$$\Delta P = \frac{1 - \varepsilon}{\varepsilon_g} * \left( \frac{\rho_g * u_g * d_p * \varepsilon}{\mu_g * (1 - \varepsilon)} \right)^{-0.37} * \frac{0.5 * \rho_g * u_g^2}{d_p} * L \quad (1.81)$$

The pressure drop over the reactor system is relatively low with:

$$\Delta P = \frac{1 - 0.5}{0.48} * \left( \frac{40 * 0.2 * 0.005 * 0.5}{2 * 10^{-5} * (1 - 0.5)} \right)^{-0.37} * \frac{0.5 * 40 * 0.2^2}{0.005} * 14.5 = 2.15 * 10^4 Pa$$

The other reactor systems will all have higher pressure drops, because they have narrower tubes or longer tube lengths. The only exception to this is the option with a lot of wide tubes and a short reactor.

1.1.6.13. Final design

The final design of the reactor characteristics is shown in Table 75.

Table 75: Reactor overview

Parameter	Value
Inlet superficial gas velocity	0.2 m/s
Inlet superficial liquid velocity	0.0072 m/s
Cooling temperature/Inlet temperature	120°C
Void fraction in the reactor	0.5
Reactor tube diameter	0.065 m
Reactor tube length	14.5 m
Amount of tubes for reaction	1575
Amount of tubes needed	1969
Particle diameter in the reactor	0.005 m
Maximum temperature in the reactor	129.6°C
Conversion over the reactor	92.7%
Production	461 kton DMC/year
Pressure drop	$2 \cdot 10^4$ Pa
Amount of shells for reaction	8
Amount of shells needed	10

## Appendix J Chapter 10 - Safety

### Appendix J.1. Safety

#### J.1.1. Fire and explosion index

The fire and explosion index was evaluated for several units to illustrate the dangers in the system. The systems that were evaluated are the reactor and some of the distillation columns. These units are generally the most dangerous in the process because of reactions and added heat, that is why these were chosen. The risk with these units is never extraordinary high according to the fire and explosion index because the process is not extremely exothermic and the distillation columns are expected to have a relatively low amount of liquid in the system at one time. The sheets are shown in Figure 124, Figure 125, Figure 126 and Figure 127.

In the following sections the F&EI indices for the different units are explained in more detail.

##### *J.1.1.1. Reactor*

The most dangerous material for the material factor is methanol. So this is chosen with a material factor of 16.

The reaction in the reactor is an exothermic esterification reaction and this gives a penalty for the F1 (0.5). It is also one of the more dangerous parts of our plant and thus it should be very accessible and thus the penalty for the accessibility is relatively low (0.2). The drain and spillage control will be with water available, but no special dike will be put around the unit (0.5). This leads to an F1 of 2.2.

The most toxic material in the reactor is expected to be 2-cyanopyridine. This does not have a NH value. But its value is expected to be 3, derived from its MSDS (0.6). The reactor operating pressure of 30 bar results in a penalty of 1 for the pressure in the system. There is also a reasonably big amount of flammable material in the system at once; with an expected residence time in the reactor of 10 minutes the penalty for this is 0.65. There are no corrosive materials inside the reactor and there are also no specific leak sensitive spots. But it is always possible and especially corrosion will always occur. Due to this a penalty of 0.1 for each of those has been taken. This leads to a F2 of 3.45.

$$F1 * F2 * MF = 121.4 = F\&EI \text{ reactor} \quad (J.82)$$

This means that there is an intermediate risk for this unit and that it should be taken under high surveillance. This system is also in contact with a lot of inert gas during operation. This lowers the chances of a hazard because the compounds can be purged with the carbon dioxide when the reactor runs out of control. However caution should be taken with people in the vicinity of the reactor for carbon dioxide poisoning. However this only works for ignition cases and not for a runaway reaction inside the reactor.

Emergency power and a diesel water pump for the cooling in case of an emergency will be used. These utilities will lower the F&EI. Also over pressure vents and rupture disks will be installed on the reactor. This results in a reduction of the F&EI of:

$$0.98 * 0.94 * 0.98 * 121.4 = 109.6 \quad (J.83)$$

This results in a radius of exposure of 33.4 meter.

#### *J.1.1.2. Phenol extractive distillation*

The most dangerous material for the material factor is methanol. So this is chosen with a material factor of 16.

The distillation only has penalties for accessibility and drainage and spillage control. For both not really much is needed to be done and thus the maximum penalties are taken for both (0.35 + 0.5). Two access roads to the column and water for fires will be added anyway of course. This leads to an F1 value of 1.85.

The NH value for phenol is 4 and thus this is the most toxic component in this distillation column (0.8). There are also relatively little compounds in the system due to the low residence time, this leads to a penalty for flammable species of 0.35. As for the reactor there are no corrosive species in the system and there are no specific leak weak spots, but both are still possible and thus a penalty of 0.1 is taken for both. This leads to a F2 of 2.35.

$$F1 * F2 * MF = 69.6 = F\&EI \text{ phenol extractive distillation column} \quad (J.84)$$

This represents a moderate risk for this distillation column. However the risks are also reduced by having the emergency fire water supply and power available. This reduces the risk to:

$$0.94 * 0.98 * 69.6 = 64.1 \quad (J.85)$$

This results in an area of exposure of: 16.4 meter.

#### *J.1.1.3. Azeotropic mixture distillation*

The most dangerous material for the material factor is methanol. So this is chosen with a material factor of 16.

The distillation only has penalties for accessibility and drainage and spillage control. For both not really much is needed to be done and thus the maximum penalties are taken for both (0.35 + 0.5). Two access roads to the column and water for fires will be added anyway of course. This leads to an F1 value of 1.85.

The most dangerous NH value in the mixture is 2 from methanol (0.4). The flows through this column are relatively low and thus the penalty for flammable liquids is 0.25. The minimum penalties for corrosion and leaking are applied again (2\*0.1). This leads to a F2 of 1.85.

$$F1 * F2 * MF = 54.76 = F\&EI \text{ azeotropic mixture distillation column} \quad (J.86)$$

This distillation column has the lowest degree of hazard for the evaluated units. It has a light risk. The Hazop analysis is also done for this column. This allows for a factor of 0.94 times the F&EI due to better risk understanding, also the emergency fire water and generator can be used for this system and thus the overall F&EI becomes:

$$0.98 * 0.94 * 54.76 = 47.4 \quad (J.87)$$

This results in an area of exposure of: 12.1 meter.

#### *J.1.1.4. Vacuum distillation column*

The most dangerous material for the material factor is methanol. So this is chosen with a material factor of 16.

The distillation only has penalties for accessibility and drainage and spillage control. For both not really much is needed to be done and thus the maximum penalties are taken for both (0.35 + 0.5). Two access roads to the column and water for fires will be added anyway of course. This leads to an F1 value of 1.85.

The compounds in this reactor are the same as in the reactor and thus the most toxic compound is again 2-cyanopyridine with a NH of 3 (0.6). The system works under partial vacuum and the penalty for that is 0.5. Also the amount of flammable compounds in this system per hour is about the same as in the reactor. But the residence time is expected to be much lower and thus the penalty for total flammable compounds in the column is lower than in the reactor (0.3). There are again no corrosive materials present in the unit, but air can always corrode the column and leaks can always occur that is for both the minimum penalties are chosen (2\*0.1). This leads to a F2 of 64.5.

$$F1 * F2 * MF = 64.5 = F\&EI \text{ vacuum distillation column} \quad (J.88)$$

This represents a moderate degree of hazard. However the risks are also reduced by having the emergency fire water supply and power available. This reduces the risk to:

$$0.94 * 0.98 * 64.5 = 59.4 \quad (J.89)$$

Which reduces the degree of hazard to light and the radius of exposure reduces to 15.2 meter.









### J.1.2. Chemical exposure index

The chemical exposure index can be determined for the methanol and phenol in the system. This is done with the following equation:

$$CEI = 655.1 \sqrt{\frac{AQ}{ERPG - 2}} \quad (J.90)$$

In which the AQ is the airborne quantity that is released into the atmosphere. The ERPG factor is a factor which represents the danger to the environment from a certain distance. This can also be used to calculate the distance you need to be away from the hazard to ensure that you are not exposed to the concentrations in the ERPG varieties. This is done with the (very similar to CEI) following equation:

$$HD = 6551 \sqrt{\frac{AQ}{ERPG}} \quad (J.91)$$

In which the ERPG represents the concentration that you want to know (-1,-2,-3) and HD the distance from the hazard that that concentration is present.

The airborne quantity can be calculated as a function of the diameter of the rupture hole, pressure of the vessel, molar weight of the released compound and the temperature of the ruptured vessel. This airborne quantity is calculated in kg/s with the following equation:

$$AQ = 4.751 * 10^{-6} * D^2 * P * \sqrt{\frac{MW}{T + 273}} \quad (J.92)$$

The tube after the reactor is investigated for the chemical exposure index for tube rupture, because this is one of the only units that it under high pressure with lots of hazardous chemicals in it. The diameter of this tube is estimated to be 14 cm based on the volume flow through it of 237 m<sup>3</sup>/h. The pressure is 30 bar and the test is done for methanol, so the molar weight is 32.04. This results in the following airborne quantity:

$$AQ = 4.751 * 10^{-6} * 0.14^2 * 30 * 10^5 * \sqrt{\frac{32.04}{120 + 273}} = 0.0798 \quad (J.93)$$

This relatively low airborne quantity results in a relatively low chemical exposure index:

$$CEI = 655.1 * \sqrt{\frac{0.0798}{1310}} = 5.11 \quad (J.94)$$

The safety distances in case of an exposure are:

Table 76: Chemical exposure index values

Risk	ERPG value	Distance (m)
All individuals can stand at this distance for 1 hour without developing life threatening health effects (ERPG-3)	6551	$HD = 6551 * \sqrt{\frac{0.0798}{6551}} = 22.86$
Persons should be able to stand at this distance for 1 hour without experiencing effects that impair the person's ability to take preventive action (ERPG-2)	1310	$HD = 6551 * \sqrt{\frac{0.0798}{1310}} = 51.1$
Persons should be able to withstand this for an hour without any serious health effects (ERPG-1)	262	$HD = 6551 * \sqrt{\frac{0.0798}{262}} = 114.3$

## Appendix K Chapter 11 - Heat Integration

### Appendix K.1. Heat Integration

Table 77: All suitable equipment for heat integration and their important parameters

<b>Name</b>	<b>Duty (kW)</b>	<b>T<sub>in</sub></b>	<b>T<sub>out</sub></b>	<b>Requires</b>	<b>ΔT</b>	<b>F x Cp (kW/k)</b>
<b>E-CL-2071</b>	-4.03E+03	120	20	Cooling	100	-4.03E+01
<b>E-CL-20710</b>	-3.25E+01	89	40	Cooling	49	-6.64E-01
<b>E-CL-2072</b>	-1.21E+03	52	20	Cooling	32	-3.77E+01
<b>E-CL-2073</b>	-9.38E+02	137	85	Cooling	52	-1.80E+01
<b>E-CL-2074a</b>	-7.77E+01	120	45	Cooling	75	-1.04E+00
<b>E-CL-2074b</b>	-6.59E+01	122	60	Cooling	62	-1.06E+00
<b>E-CL-2074c</b>	-2.76E+02	133	20	Cooling	113	-2.44E+00
<b>E-CL-2075</b>	-3.42E+03	223	120	Cooling	103	-3.32E+01
<b>E-CL-2076a</b>	-6.15E+02	128	40	Cooling	88	-6.99E+00
<b>E-CL-2076b</b>	-7.55E+02	146	40	Cooling	106	-7.13E+00
<b>E-CL-2076c</b>	-3.70E+02	144	95	Cooling	49	-7.56E+00
<b>E-CL-2077</b>	-4.59E+02	124	65	Cooling	59	-7.78E+00
<b>E-CL-2078</b>	-7.56E+02	95	40	Cooling	55	-1.37E+01
<b>E-CL-2079</b>	-4.55E+02	245	160	Cooling	85	-5.35E+00
<b>E-H-2071</b>	3.50E+03	46	147	Heating	-101	3.46E+01
<b>E-H-2072</b>	5.64E+03	31	150	Heating	-119	4.74E+01
<b>E-H-2073</b>	8.74E+02	123	150	Heating	-27	3.24E+01
<b>E-H-2074</b>	1.69E+03	117	150	Heating	-33	5.12E+01
<b>E-H-2075</b>	1.20E+02	20	50	Heating	-30	4.02E+00
<b>E-H-2076</b>	4.10E+02	21	125	Heating	-104	3.94E+00
<b>E-H-2078</b>	3.68E+03	118	150	Heating	-32	1.15E+02
<b>T-2071 Con</b>	-1.28E+03	51	50	Cooling	1	-1.28E+03
<b>T-2071 Reb</b>	3.88E+03	223	224	Heating	-1	3.88E+03
<b>T-2072 Con</b>	-6.50E+03	52	51	Cooling	1	-6.50E+03
<b>T-2072 Reb</b>	2.13E+03	95	96	Heating	-1	2.13E+03
<b>T-2073 Con</b>	-1.41E+03	137	136	Cooling	1	-1.41E+03
<b>T-2073 Reb</b>	2.59E+03	245	246	Heating	-1	2.59E+03
<b>T-2074 Con</b>	-4.71E+02	89	88	Cooling	1	-4.71E+02
<b>T-2074 Reb</b>	5.18E+02	188	189	Heating	-1	5.18E+02

## Appendix L Chapter 12 - Economics

In this chapter, the economics analysis is made over this process. First the capital expenditure (CAPEX) is determined and then the operational expenditure (OPEX) is calculated. The design of the equipment is covered in chapter 9. Certain aspects of the process are not fully known, the regeneration part for example, and instead of a very rough estimation, a sensitivity analysis is made. At the end an overview and evaluation of the economic analysis will be provided.

### Appendix L.1. CAPEX

The capital expenditure is the costs of all equipment that need to be purchased in order to operate the plant. This includes units, piping, valves, storage tanks, etc. For a detailed capital investment analysis, all these aspects need to be designed in detail. This is beyond the scope of the course and to make it less complex, only the major equipment is designed in detail. By applying the Lang factor method, the costs for all additional equipment such as In this evaluation the Lang factor is 6.[72]

$$CAPEX = f_L \sum_i C_{Pi} \quad (L.95)$$

All major equipment needs to be included in the evaluation. This means that a design is made for all heat exchangers, flash vessels, distillation columns, pumps and compressors. First the needed parameters from the design section are mentioned and then the method to estimate the cost price is given for the different possibilities.

#### L.1.1. Heat exchanger

Heat exchangers are widely present in the system. Just to cool down or heat up a stream, but also in the condenser and reboiler of a distillation column and in multistage compressors. From the design the following parameters are needed:

- Area [m<sup>2</sup>]
- Type of heat exchanger
- Tube length [ft]
- Pressure in the shell [bar]
- Material of construction [shell/tube]

##### *L.1.1.1. Shell and tube heat exchanger*

For a shell and tube heat exchanger there are multiple types: floating head, fixed head, U-tube and kettle vaporizer. The general formula for the cost estimation is given in equation (L.96).[80]

$$C_P = F_P F_M F_L \left( \frac{I_C}{I_r} \right) C_B \quad (L.96)$$

The base costs for a heat exchanger ( $C_B$ ) is different for each type and the size factor is the required heat exchange area in ft<sup>2</sup>. Equations (L.97), (L.98), (L.99) and (L.100) are used as costs estimates for the different types of heat exchangers.[80]

$$\text{Floating head} \rightarrow C_B = \exp(11.667 - 0.8709(\ln(A)) + 0.09005(\ln(A))^2) \quad (\text{L.97})$$

$$\text{Fixed head} \rightarrow C_B = \exp(11.0545 - 0.9228(\ln(A)) + 0.09861(\ln(A))^2) \quad (\text{L.98})$$

$$U - \text{Tube} \rightarrow \exp(11.147 - 0.9228(\ln(A)) + 0.09790(\ln(A))^2) \quad (\text{L.99})$$

$$\text{Kettle vaporizer} \rightarrow \exp(11.967 - 0.8709(\ln(A)) + 0.09005(\ln(A))^2) \quad (\text{L.100})$$

These equations result in the base costs of the heat exchanger and are valid between an area of 150 to 12,000 ft<sup>2</sup>. The tubes are made from carbon steel and 20 ft long. In the carbon steel shell the pressure range is up to 100 psig (~11 bar). Any deviations from this base case result in a penalty factor, present in the cost equation as  $F_M$ ,  $F_P$  and  $F_L$ . To compare the prices for the different heat exchanger types, Figure 128 is made. It can be seen that fixed head and U-tube heat exchangers are the cheapest. Followed by the floating head and a kettle vaporizer is the most expensive one.[80]

The base costs are based on estimations with a CEPCI (Chemical Engineering Plant Cost Index) of 500 ( $I_r$ ), where the actual CEPCI is 576 ( $I_c$ ). Therefore the purchase price has to be correction by this ratio.

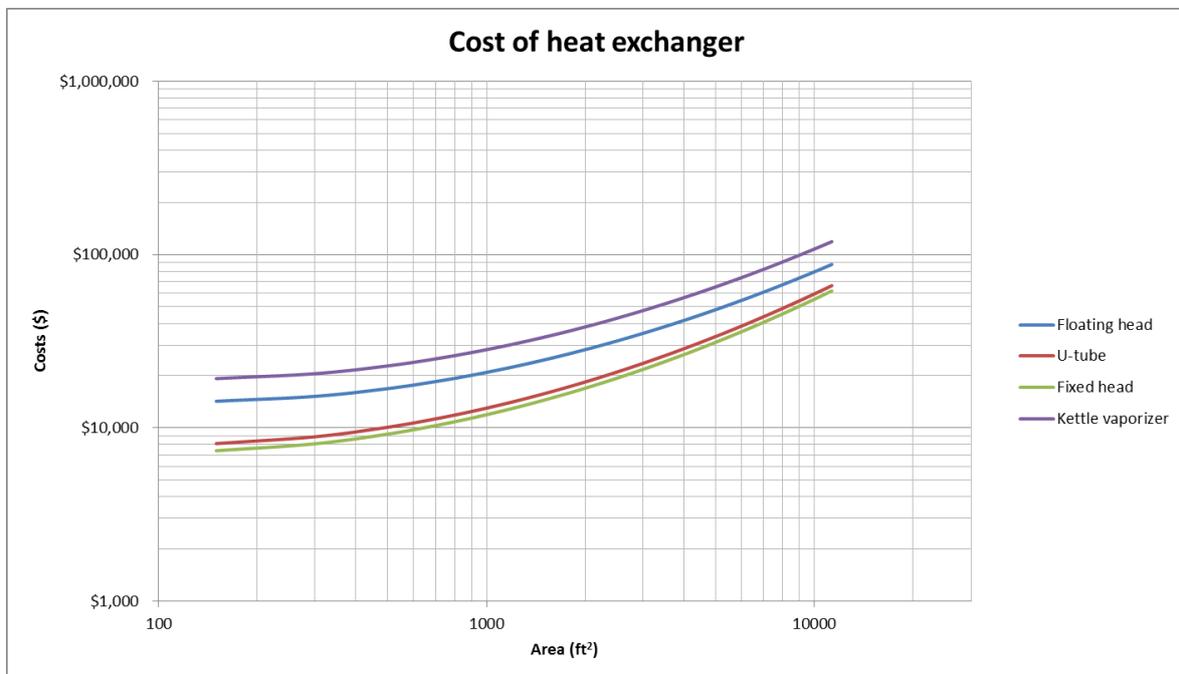


Figure 128: Base costs for shell and tube heat exchangers

#### L.1.1.1.1. Tube length correction

When a tube length is desired of less than 20 ft, some standard tube lengths are available. However, 20 ft is the most common size and therefore all deviations will increase the total price. In Table 78 a list of available tube lengths is provided with their respective length factor.[80]

Table 78: Tube length factor for shell and tube heat exchangers

Tube length (ft)	$F_L$
8	1.25
12	1.12
16	1.05
20	1.00

L.1.1.1.2. Pressure correction

The base case heat exchanger is applicable to a pressure of 100 psig. For higher pressure the price will go up and this is given with the pressure correction factor. To calculate this factor, equation (L.101) can be used with a maximum of 2000 psig. [80]

$$F_p = 0.9803 + 0.018 \left( \frac{P}{100} \right) + 0.0017 \left( \frac{P}{100} \right)^2 \quad (L.101)$$

L.1.1.1.3. Material correction

Carbon steel is the basic material to construct a shell and tube heat exchanger. For some compounds or operation conditions this might not be a suitable material, however. When a different material is chosen for either the shell or the tube this results in a price penalty given in equation (L.102), where A is the heat exchanger area in ft. The parameters for the equation are listed in Table 79.[80]

$$F_M = a + \left( \frac{A}{100} \right)^b \quad (L.102)$$

Table 79: Available shell and tube materials

Material of construction		
Shell/tube	a	b
CS/CS	0	0
CS/brass	1.08	0.05
CS/SS	1.75	0.13
CS/Monel	2.1	0.13
CS/titanium	5.2	0.16
CS/Cr-Mo	1.55	0.05
Cr-Mo/Cr-Mo	1.7	0.07
SS/SS	2.7	0.07
Monel/Monel	3.3	0.08
Titanium/titanium	9.6	0.06

L.1.1.2. Double-pipe heat exchanger

For a heat exchange surface area less than 200 ft<sup>2</sup> a double-pipe heat exchanger is the better option. Even for a surface area as low as 2 ft<sup>2</sup> these are applicable, in contrast to the shell and tube heat exchangers with a minimum of 150 ft<sup>2</sup>. [80]

The general equation to calculate the costs is similar to a shell and tube heat exchanger, but there is no length factor present, because there is only one outer and one inner pipe.[80]

$$C_p = F_p F_M \left( \frac{I_c}{I_r} \right) C_B \quad (L.103)$$

Equation (L.104) will be used to estimate the base costs of the double-pipe heat exchanger (CEPCI = 500). This holds for pressures until 600 psig and both tubes made of carbon steel. A graph of the costs as function of the area is given in Figure 129.[80]

$$C_B = \exp(7.1460 + 0.16 \ln(A)) \quad (L.104)$$

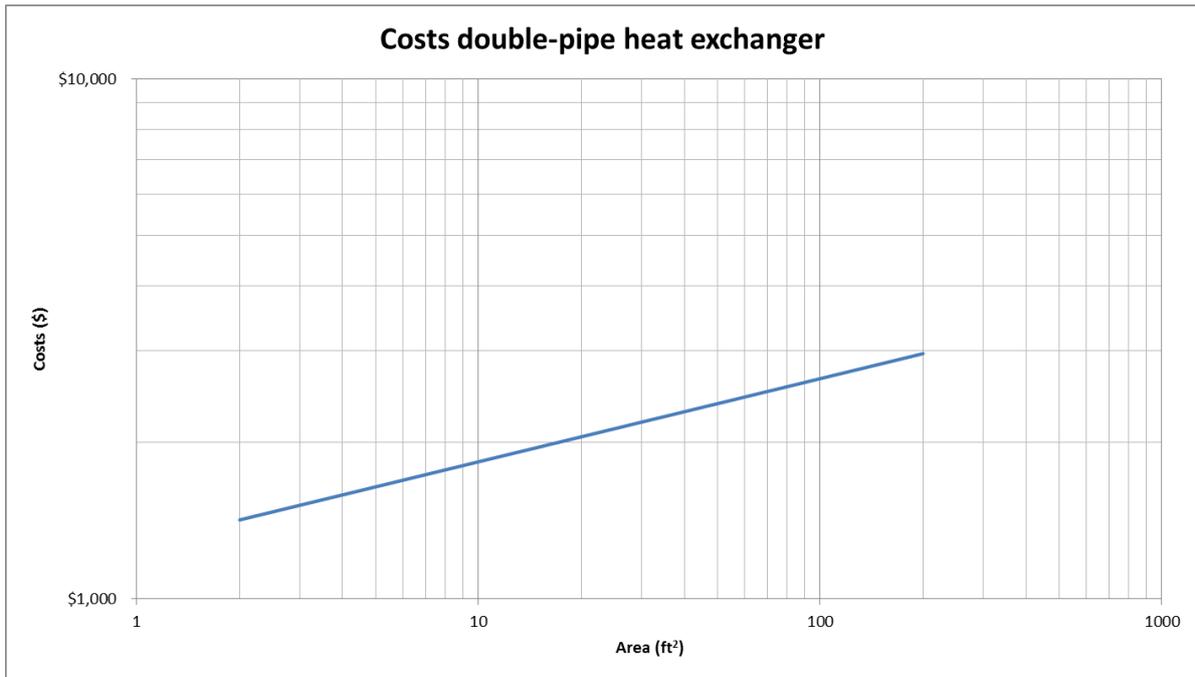


Figure 129: Base costs of a double-pipe heat exchanger

L.1.1.2.1. Pressure correction

A base case double-pipe heat exchanger is applicable for a pressure up to 600 psig. For a higher pressure, the following correlation is used to estimate the additional costs:[80]

$$F_p = 0.8510 + 0.1292 \left( \frac{P}{600} \right) + 0.0198 \left( \frac{P}{600} \right)^2 \quad (\text{L.105})$$

The correlation is valid for pressures between 600 and 3000 psig.

L.1.1.2.2. Material correction

As for a shell and tube heat exchanger, a different materials of construction result in a price penalty. The list of materials is not as large though, as shown in Table 80.[80]

Table 80: Material factors for a double-pipe heat exchanger

Material	$F_M$
CS/CS	1.0
CS/SS	2.0
SS/SS	3.0

L.1.1.3. Summary heat exchangers

Input data from Table 18 in chapter 9 is used to calculate the costs for every heat exchanger. The results are given in Table 81. The total costs for heat exchangers in the process, without applying the Lang factor is estimated at \$ 556,000,-.

Table 81: Summary of purchase costs for the heat exchangers in the process

Name	Type	Pshell [bar]	A [m <sup>2</sup> ]	Material [shell/tube]	Tube length [ft]	Price (\$)
CL-2071	U-tube	30.0	648.39	CS/CS	20	\$ 54,707.61
CL-20710	Double-pipe	1.0	4.72	CS/CS	20	\$ 2,740.81
CL-2072	U-tube	1.0	184.36	CS/CS	20	\$ 21,118.89
CL-2073	U-tube	10.0	22.32	CS/CS	20	\$ 9,911.18
CL-2074a	Double-pipe	2.4	13.89	CS/CS	20	\$ 3,257.56
CL-2074b	Double-pipe	5.0	8.81	CS/CS	20	\$ 3,028.59
CL-2074c	U-tube	10.2	41.10	CS/CS	20	\$ 11,305.09
CL-2075	U-tube	1.4	89.79	CS/CS	20	\$ 14,762.56
CL-2076a	U-tube	3.0	178.61	CS/CS	20	\$ 20,744.05
CL-2076b	U-tube	8.3	188.65	CS/CS	20	\$ 21,424.11
CL-2076c	U-tube	23.5	31.12	CS/CS	20	\$ 11,076.46
CL-2077	U-tube	0.7	29.94	CS/CS	20	\$ 10,391.37
CL-2078	U-tube	1.2	162.08	CS/CS	20	\$ 19,660.22
CL-2079	Double-pipe	10.0	9.33	SS/SS	20	\$ 9,169.93
H-2071	U-tube	11.4	297.42	CS/CS	20	\$ 30,777.91
H-2072	U-tube	11.4	92.94	CS/CS	20	\$ 15,152.36
H-2073	U-tube	11.4	24.41	CS/CS	20	\$ 10,103.94
H-2074	U-tube	11.4	44.88	CS/CS	20	\$ 11,636.26
H-2075	Double-pipe	4.5	1.43	CS/CS	20	\$ 2,264.12
H-2076	Double-pipe	4.5	9.03	CS/CS	20	\$ 3,040.34
H-2078	U-tube	11.4	98.53	CS/CS	20	\$ 15,547.10
T-2071 Con	U-tube	0.3	187.25	CS/CS	20	\$ 21,306.69
T-2071 Reb	U-tube	32.0	16.78	CS/CS	20	\$ 10,403.53
T-2072 Con	U-tube	1.0	864.45	CS/CS	20	\$ 70,318.08
T-2072 Reb	U-tube	4.5	41.00	CS/CS	20	\$ 11,216.21
T-2073 Con	Double-pipe	10.0	16.78	SS/SS	20	\$ 10,072.57
T-2073 Reb	U-tube	42.0	326.74	CS/SS	20	\$ 115,626.89
T-2074 Con	Double-pipe	1.0	10.93	SS/SS	20	\$ 9,405.09
T-2074 Reb	Double-pipe	32.0	10.58	CS/SS	20	\$ 6,237.33
<b>Total</b>						\$ 556,406.85

### L.1.2. Pressure vessel

Pressure vessels are widely used in the chemical industry. A distinction is made between horizontal vessels, vertical vessels and towers. Applications for horizontal and vertical vessels include reflux drums, flash drums, knock-out drums, settlers, reactors, mixing vessels and storage drums. The towers are used for distillation, adsorption, absorptions and stripping. In this section only the costs for an empty vessel are estimated. The internals are covered in section L.1.3..

The base costs include nozzles, manholes and supports, but not the platforms and ladders. These are additional costs. In general the following equation is used, where  $C_B$  are the base costs and  $C_{PL}$  are costs of platforms and ladders:[80]

$$C_P = (F_M C_B + C_{PL}) \left( \frac{I_c}{I_r} \right) \quad (\text{L.106})$$

For every vessel type the factor that determines the price is the weight of the column. Equation (L.107) is an approximation of the weight of a cylindrical vessel with 2:1 elliptical heads. With  $t_s$  as the wall thickness of the shell.[80]

$$W = \pi(D_i + t_s)(L + 0.8D_i)t_s\rho \quad (\text{L.107})$$

The material factor in eq. (L.106) is the same for all pressure vessels and can be found in Table 82.[80]

*Table 82: Material factor for pressure vessels*

<b>Material</b>	<b><math>F_M</math></b>
Carbon steel	1.0
Low-Alloy steel	1.2
Stainless steel 304	1.7
Stainless steel 316	2.1
Carpenter 20CB-3	3.2
Nickel-200	5.4
Monel-400	3.6
Inconel-600	3.9
Incoloy-825	3.7
Titanium	7.7

In the design, the following parameters need to be determined:

- Vessel type
- Operating pressure
- Operating temperature
- Vessel length
- Vessel diameter

#### *L.1.2.1. Horizontal vessel*

First the costs for a horizontal pressure vessel are estimated. There are some horizontal vessels present in the process as flash vessels. Parts of the steps are similar for vertical vessels, towers and vessels under vacuum.

To determine the weight of the vessel the thickness of the wall is needed. This requires slightly different methods for the different vessel types.

The wall thickness to withstand the pressure inside the vessel can be calculated with equation (L.108) and is valid if the inside pressure is higher than the outside pressure.[80]

$$t_p = \frac{P_d D_i}{2SE - 1.2P_d} \quad (\text{L.108})$$

S is the maximum allowable stress in psi, E is the weld efficiency and  $P_d$  is the design pressure.

The design pressure is always larger than the operating pressure. For an operating pressure lower than 5 psig, a design pressure of 10 psig is taken. For pressures higher than 1,000 psig, the design pressure is 10% higher. If the operating pressure is in between, equation (L.109) is used to determine the design pressure.[80]

$$P_d = \exp(0.60608 + 0.91615 \ln P_o + 0.0015655(\ln P_d)^2) \quad (\text{L.109})$$

The weld efficiency depends on the wall thickness. For a wall thickness lower than 1.25 in. a weld efficiency of 0.85 should be used and for larger wall thicknesses a weld efficiency of 1.0 is sufficient. Because the wall thickness is not known yet, a value is guessed for E and later on checked whether the first guess is justified.[80]

The maximum allowable stress is different for each temperature. A higher temperature means a lower maximum allowable stress. As for the pressure, the design temperature is higher than the operating temperature. The design temperature is taken as 50°F higher than the operating temperature. Until 650°F, carbon steel can be used, for temperatures up to 900°F low-alloy steel is most suitable. The maximum allowable stress is given in Table 83.[80]

Table 83: Maximum allowable stress as function of the design temperature

Temperature (°F)	Maximum allowable stress (psi)
-20 to 650	15,000
700	15,000
750	15,000
800	14,750
850	14,200
900	13,100

Besides the pressure resistance of the vessel, an extra corrosion allowance has to be taken into account, even for non-corrosive conditions. This extra allowance is 1/8 in. The total diameter of the horizontal vessel is:[80]

$$t_s = t_p + t_c \quad (L.110)$$

Now the price of the vessels can be determined. Two correlations are needed, one for the vessel itself ((L.111)) and one for the platforms and ladders ((L.112)). The weight is in lb and valid between 1,000 and 920,000 lb. The diameter is in ft. and applicable in the range of 3 to 12 ft.[80]

$$C_B = \exp(8.9552 - 0.2330 \ln W + 0.04333(\ln W)^2) \quad (L.111)$$

$$C_{PL} = 2,005(D_i)^{0.20294} \quad (L.112)$$

#### L.1.2.2. Vertical pressure vessel

A vertical pressure vessel is applied in the DMC process for a flash vessel. The first part of the cost evaluation is similar to a horizontal pressure vessel.

Until the maximum allowable stress, the method in the previous section can be followed. However, equation (L.108) does not account for the effect of wind or an earthquake on a vertical vessel or tower. An additional thickness need to be applied at the bottom of the column. This can be determined with:[80]

$$t_w = \frac{0.22(D_o + 18)L^2}{SD_o^2} \quad (L.113)$$

The outer diameter can only be known as the wall thickness is known. Therefore an iterative approach is used. First the wall thickness is guessed and checked if it is equal to the obtained wall thickness at the end of the calculations. Then the average vessel wall thickness can be determined with:[80]

$$t_V = \frac{t_p + (t_p + t_w)}{2} \quad (L.114)$$

As for the vertical vessel, a corrosion allowance of 1.8 in. is applied to obtain the final wall thickness.[80]

$$t_s = t_v + t_c \quad (L.115)$$

Then the price of the vertical pressure vessel is determined with a correlation for the empty vessel and for the platforms and ladders. The base costs correlation is valid for vessel between 4,200 and 1,000,000 lb. (L.117) is valid for  $3 < D_i < 21 \text{ ft}$  and  $12 < L < 40 \text{ ft}$ .[80]

$$C_B = \exp(8.9552 - 0.2330 \ln W + 0.4333(\ln W)^2) \quad (L.116)$$

$$C_{PL} = 361.8(D_i)^{0.73960}(L)^{0.70684} \quad (L.117)$$

#### L.1.2.3. Tower

A tower is just a large vertical pressure vessel and the correlations are valid over a wider range of diameter, length and weight. Until the price correlations, the method is similar to a vertical pressure vessel. Correlations to estimate the costs are given in equation (L.118) and (L.119).[80]

$$C_B = \exp(7.2756 + 0.18255 \ln W + 0.02297(\ln W)^2) \quad (L.118)$$

$$C_{PL} = 300.9(D_i)^{0.63316}(L)^{0.80161} \quad (L.119)$$

These correlations have the following ranges:  $9,000 < W < 2,500,000 \text{ lb}$  ,  $3 < D_i < 12 \text{ ft}$  and  $27 < L < 170 \text{ ft}$ .[80]

#### L.1.2.4. Vacuum vessel

A vacuum vessel is not a special type of vessel. The cost correlations for the horizontal, vertical and tower are applied. Only when the operating pressure is below the atmospheric pressure, equation (L.108) does not apply anymore. Therefore the only difference is the determination of the wall thickness.

The method is based on the length to diameter ratio and modulus of elasticity of the wall. [80]

$$t_E = 1.23D_o \left( \frac{P_d L}{E_M D_o} \right)^{0.4} \quad (L.120)$$

This value needs to be corrected, by adding  $t_{EC}$  to it.

$$t_{EC} = L(0.18D_i - 2.2) * 10^{-5} - 0.19 \quad (L.121)$$

As the outer diameter is a function of the wall thickness, here as well an iterative approach is needed. The design pressure can be taken as the difference between the operating pressure and atmospheric pressure. For the modulus of elasticity a table is provided for carbon steel and low-alloy steel at different temperatures (Table 84).[80]

Table 84: Modulus of elasticity (multiply by 106)

Temperature (°F)	Carbon steel	Low-alloy steel
-20	30.2	30.2
200	29.5	29.5
400	28.3	28.6
650	26.0	27.0
700	-	26.6
800	-	25.7
900	-	24.5

Only the correction for the corrosion of 1/8 in. has to be applied and then the total wall thickness a vacuum vessel is estimated. For the price calculation, the correlations in the previous sections are applicable.

#### L.1.2.5. Summary pressure vessel

A distinction can be made between horizontal vessels, vertical vessels and towers. All have different price estimation correlations. In the previous sections, a method is provided to estimate this price. For a pressure below atmospheric, the wall thickness has to be determined in a different way. The base costs, without platforms and ladders can be compared in Figure 130.

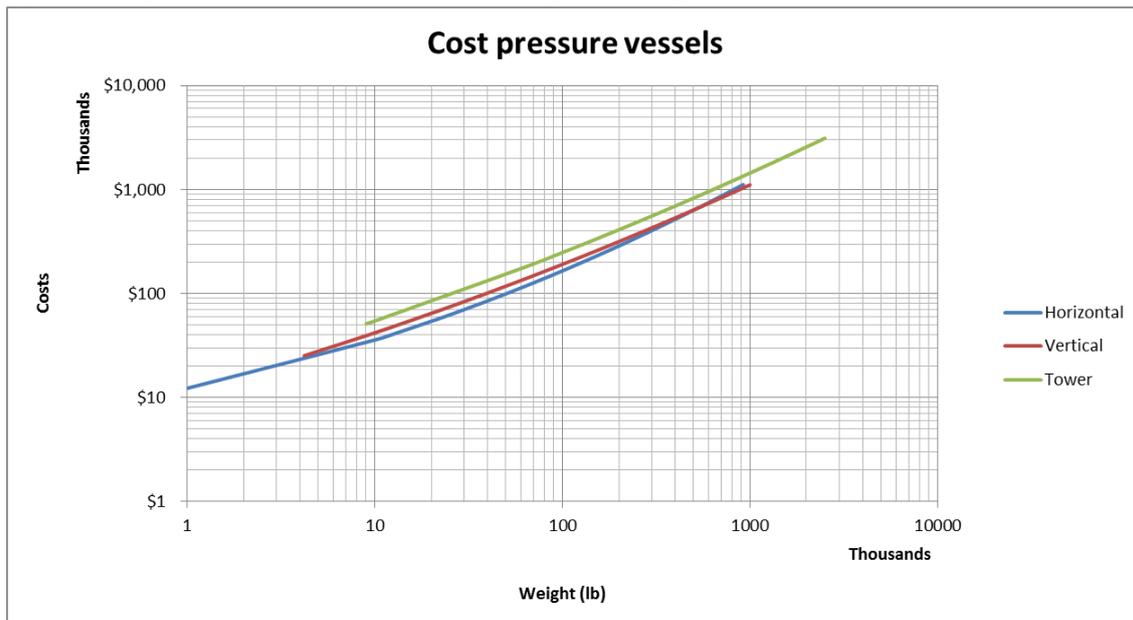


Figure 130: Costs comparison between pressure vessels

Price estimation for the flash vessels is in the process are carried out via the method described above. In total two horizontal and two vertical flash vessels are present. A summary of the cost estimation for the flash vessels is given in Table 85. All four flash vessels combined will cost about \$460,000,-. Some dimensions of the vessels are outside the applicable ranges for the cost estimation. The equations are therefore extrapolated beyond their application range and this will probably decrease the accuracy of the cost price estimation.

Table 85: Summary of the costs estimation for the flash vessels

Name	Type	Po [bar]	To [°C]	Length [m]	Diameter [m]	Price (\$)
F-2071	Vertical	30.00	120.00	7.86	3.99	\$ 373,192.37
F-2072	Vertical	29.80	20.00	3.79	1.34	\$ 60,364.58
F-2073	Horizontal	0.80	20.00	3.00	1.00	\$ 18,621.27
F-2074	Horizontal	10.00	20.00	1.80	0.60	\$ 14,241.47
<b>Total</b>						<b>\$ 466,419.69</b>

Distillation columns also consist of a pressure vessel, an overview of costs is given in Table 89 at the end of the section about vessel internals.

### L.1.3. Vessel internals

Some unit operations require some kind of internals inside a vessel, think about distillation, stripping or absorption. The costs for the vessel can be calculated from the previous section, but the internals are separately covered in this section.

Two kind of internals will be discussed here, plates and packing.

#### L.1.3.1. Plates

To approximate the cost price for plates, the following data is needed:

- Number of trays
- Type of trays
- Material of the trays

The costs for plates can be determined with equation (L.122). It is build up from base costs for trays and correction factors for the type of tray, material and the number of trays. The base case is defined by sieve trays made of carbon steel with the total number of trays more than 20. This includes downcomers and installation.[80]

$$C_P = N_T F_{NT} F_{TT} F_{TM} \left( \frac{I_c}{I_r} \right) C_B \quad (L.122)$$

The base costs, with a CEPCI of 500, can be estimated by:[80]

$$C_B = 468 \exp(0.1739D_i) \quad (L.123)$$

When the number of trays is lower than 20, the total installation costs will increase. So for  $N_T \leq 20$ , the correction factor  $F_{NT} = 1$ . For more than 20 trays, the correction factor will be:[80]

$$F_{NT} = \frac{2.25}{1.0414^{NT}} \quad (L.124)$$

In general there are three types of trays. Sieve trays, valve trays and bubble cap trays. A sieve tray is the most simple to construct and therefore taken as base. In case a valve or bubble cap is used, the price will go up with the factors shown in Table 86.[80]

Table 86: Correction factor for the type of trays

Tray type	$F_{TT}$
Sieve	1.00
Valve	1.18
Bubble cap	1.87

The last correction factor is for the material of construction. Carbon steel is the base material, but with the presence of corrosive materials other materials might be beneficial. The correction factor for these more expensive materials are a function of the inner diameter of the vessels.[80]

Table 87: Material factor for the trays

Material	$F_{TM}$
Carbon steel	1.0
303 Stainless steel	$1.189+0.0577D_i$
316 Stainless steel	$1.401+0.0724D_i$
Carpenter 20CB-3	$1.525+0.0788D_i$
Monel	$2.306+0.1120D_i$

L.1.3.2.Packing

Packing is more efficient in terms of separation than plates. The drawback is the higher costs. For the cost estimation, two types of packing are identified; dumped packing and structured packing. From the design, the following parameters are needed:

- Type of packing
- Packing length
- Number of liquid distributors

The general cost equation for packing is given below:[80]

$$C_P = (V_P C_{PK} + C_{DR}) \left( \frac{I_c}{I_r} \right) \quad (L.125)$$

Liquid distributors are needed in a packed column to make sure liquid is present everywhere. If there is no information from the vendor, the distributor price ( $C_{DR}$ ) is \$125/ft<sup>2</sup>. Where the area is the cross-sectional area of the vessel. The cost for packing is given in \$/ft<sup>3</sup> and therefore the packing volume is needed.[80]

L.1.3.2.1. Dumped packing

Dumped packing is cheaper than a structured packing, but is less efficient in terms of height equivalent of a theoretical stage and pressure drop. Dumped packing is available in a wide variety of types, sizes and materials. Table 88 gives an overview of some dumped packings, with the installed costs per cubic feet of vessel.[80]

Table 88: Installed costs for dumped packings

Size	Installed costs (\$/ft <sup>3</sup> )				
	1 in.	1.5 in.	2 in.	3 in.	4 in.
Berl Saddles					
<i>Ceramic</i>	48	37	28		
Raschig rings					
<i>Carbon steel</i>	54	40	34	26	
<i>Stainless steel</i>	180	139	110	63	
<i>Ceramic</i>	26	21	19	15	
Intalox saddles					
<i>Ceramic</i>	34	28	24	19	
<i>Polypropylene</i>	37		23	12	
Pall rings					
<i>Carbon steel</i>	49	37	32		
<i>Stainless steel</i>	168	129	110		
<i>Polypropylene</i>	37	26	21	16	
Cascade mini-rings					
<i>Stainless steel</i>	134		95	70	52
<i>Ceramic</i>	90		70	56	
<i>Polypropylene</i>	90		70	56	
Tellerettes					
<i>Polyethylene</i>	76				

#### L.1.3.2.2. Structured packing

The cost estimation for structured packing depends highly on the type of packing. Without any information from the vendor it is hard to make an accurate estimate. For corrugated-sheet packing made of stainless steel, a installed costs of \$250/ft<sup>3</sup> is taken.[80]

#### L.1.3.3. Summary vessel internals

So there are two types of vessel internals available, plates and packing. In the DMC process, this is used as internals for distillation column.

A distillation column is a combination of a pressure vessel and vessel internal, so the costs of both parts are added to obtain the total costs. A summary of the distillation columns is given in Table 89.[80]

Table 89: Costs of the distillation columns

Number	Internal	Diameter [m]	Height [m]	To [°C]	Po [bar]	NT
T-2071	Packing	3.41	6.86	223.2	0.5	-
T-2072	Plate	2.72	12.00	95.5	1.2	16
T-2703	Plate	0.86	21.50	224.9	10.2	35
T-2074	Plate	0.85	13.00	187.7	1.2	18
Number	Type	Material	Packing	Packing length [m]	# Distributors	Price (\$)
T-2071	-	-	Structured	2.86	2	\$ 422,973.77
T-2072	Sieve	CS	-	-	-	\$ 181,249.53
T-2703	Sieve	SS316	-	-	-	\$ 252,988.10
T-2074	Sieve	SS316	-	-	-	\$ 119,040.30
<b>Total</b>						<b>\$ 976,251.70</b>

#### L.1.4. Pump

The cost estimation of the pumps require a different method for the three types of pumps present in the process. Even the size factors for the cost estimation differ from pump to pump. All three will be discussed in this section. The pumps are driven by an electric motor, but this is not taken into account in the price estimation. Therefore a separate method is provided to calculate the additional costs for the motor.

The following parameters are obtained from the design:

- Liquid flow rate [m<sup>3</sup>/s]
- Pump head [m]
- Pump type
- Power consumption [Hp]
- Material of construction
- Motor efficiency

##### L.1.4.1. Centrifugal pump

The cost estimation of a centrifugal pump can be carried out with multiple size factors. Most common are the brake horsepower and a size factor including the capacity and the head. The latter one will be used in this project. For the size factor equation (L.126) is applied, valid between 400 and 100,000. Here the flow rate is in gallons per minute and the head in ft.[80]

$$S = Q(H)^{0.5} \quad (L.126)$$

Then the base costs of the centrifugal pump is calculated with the following correlation, with a CEPCI of 500:[80]

$$C_B = \exp(9.7171 - 0.6019 \ln S + 0.0519(\ln S)^2) \quad (\text{L.127})$$

The base costs for the centrifugal pump is then corrected with a pump type factor, material factor and the CEPCI ratio.[80]

$$C_P = F_T F_M \left( \frac{I_C}{I_r} \right) C_B \quad (\text{L.128})$$

#### L.1.4.1.1. Type factor

As can be read in chapter 9.4, there are multiple types of centrifugal pumps with different ranges in terms of head and capacity. In the equipment design the suitable pump type is selected, however every type has a type factor, which corrects the purchase costs for this specific type. Table 90 gives these factors.[80]

*Table 90: Type factor for a centrifugal pump*

<b>Type</b>	<b><math>F_T</math></b>
A	1.00
B	1.50
C	1.70
D	2.00
E	2.70
F	8.90

#### L.1.4.1.2. Material factor

The material factors for the centrifugal pump is given in Table 91. The base material is cast iron and the price can even go up almost 10 times for titanium.[80]

*Table 91: Material factors for centrifugal pumps*

<b>Material</b>	<b><math>F_M</math></b>
Cast iron	1.00
Ductile iron	1.15
Cast steel	1.35
Bronze	1.90
SS	2.30
Hastelloy C	2.95
Monel	3.30
Nickel	3.50
Titanium	9.70

#### L.1.4.2. Gear pump

The gear pump is a little less complex in terms of costs estimation. As a size factor, the liquid flow rate in gallons per minute will be used. Besides this only the CEPCI ratio and a correction for the material is applied.[80]

$$C_P = F_M \left( \frac{I_C}{I_r} \right) C_B \quad (L.129)$$

Equation (L.130) is an estimate for the base costs of a gear pump, with a CEPCI of 500. This correlation holds for flow rates from 10 to 900 gpm.[80]

$$C_B = \exp(7.6964 + 0.1986 \ln Q + 0.029(\ln Q)^2) \quad (L.130)$$

The applicable materials for a gear pump are the same as for a centrifugal pump. Also the material factors are the same. So the correction factors for the material of construction can be found in Table 91.[80]

#### L.1.4.3. Reciprocating plunger pump

A reciprocating pump has the largest operating range of all pumps. These are therefore often used in the process. The size factor for the cost estimation is the brake horsepower. A correction factor need to be used for the material and the CEPCI ratio is applied. The equation is the same as for a gear pump ((L.129)).[80]

To calculate the brake horsepower, the total power consumption obtained from the design is multiplied by the motor efficiency.[80]

$$P_B = P_C \eta_M \quad (L.131)$$

The cost equation is given in (L.132) with an application range of 1 to 200 BHp and a CEPCI of 500.

$$C_B = \exp(7.8103 + 0.26986 \ln P_B + 0.06718(\ln P_B)^2) \quad (L.132)$$

The material used in the base case is ductile iron. Other materials are listed in Table 92 with their material factor.[80]

Table 92: Material factors for a reciprocating plunger pump

Material	$F_M$
Ductile iron	1.00
Ni-Al-Bronze	1.15
Carbon steel	1.50
Stainless steel	2.20

#### L.1.4.4. Electric motor

The electric motor is needed to drive the pumps, however this is not included in the cost estimate for the pump. This means the costs for the motor have to be calculated separately and added to the pump costs.

The base cost calculation is based on the total horsepower of the pump. This includes a motor operating at 3,600 rpm with and open, drip-proof enclosure. An estimation of the costs is given with equation (L.133). It is graphically presented in Figure 131.[80]

$$C_B = \exp(5.8259 + 0.13141 \ln P_C + 0.053255(\ln P_C)^2 + 0.028628(\ln P_C)^3 - 0.0035549(\ln P_C)^4) \quad (L.133)$$

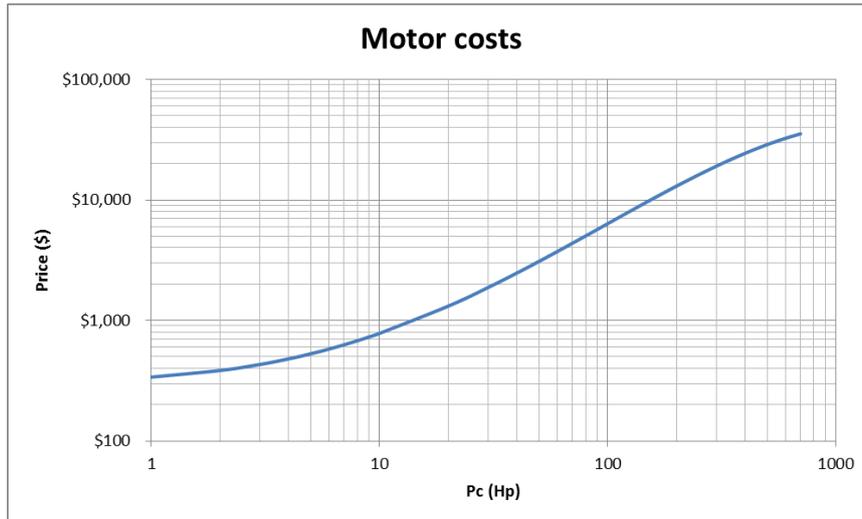


Figure 131: Costs for an electric motor

For other electric motor types a type factor has to be used and as always the CEPCI ratio.[80]

$$C_P = F_T \left( \frac{I_C}{I_r} \right) C_B \quad (L.134)$$

Table 93 can be used for the type factor. For the project all motors are designed as open, drip-proof enclosure.[80]

Table 93: Type factor for electric motors

Type motor	3,600 rpm	1,800 rpm
Open, drip-proof enclosure, 1 to 700 Hp	1.0	0.9
Totally enclosed, fan-cooled, 1 to 250 Hp	1.4	1.3
Explosion-proof enclosure, 1 to 250 Hp	1.8	1.7

#### L.1.4.5. Summary pump

In the previous section, the different types of pumps are designed. With the data obtained from the design chapter, an estimation is made from the total costs of the pumps. This does not include the Lang factor yet.

The results are given in Table 94. In total \$140,000,- will be spend on the pumps.

Table 94: Cost estimation results for the pumps in the process

Number	Flow rate [m3/s]	Head [m]	Pump type	Power [Hp]	$\eta_P$	$\eta_M$	Material	Price (\$)
P-2071	1.42E-02	378.70	Plunger	68.57	0.90	0.90	Carbon Steel	\$ 45,550.36
P-2072	1.35E-05	277.40	Plunger	1.25	0.90	0.80	Carbon steel	\$ 4,664.32
P-2073	1.53E-03	106.83	Plunger	2.66	0.90	0.82	Carbon steel	\$ 5,962.73
P-2074	1.19E-03	286.16	Plunger	4.31	0.90	0.84	Carbon steel	\$ 7,305.70
P-2075	6.88E-04	1.92	Gear	1.00	0.80	0.65	Cast iron	\$ 5,200.77
P-2077	2.11E-02	300.18	E	133.40	0.67	0.91	Cast iron	\$ 26,217.44
P-2078	2.33E-02	8.88	Gear	4.20	0.80	0.84	Cast iron	\$ 23,236.70
P-2079	2.17E-04	4.43	Plunger	1.25	0.90	0.80	Carbon steel	\$ 7,254.02
P-20710	1.89E-03	100.40	Gear	3.43	0.80	0.83	SS	\$ 14,461.83
<b>Total</b>								<b>\$ 139,853.87</b>

### L.1.5. Compressor

A compressor is used to compress a gas to a desired pressure. The ratio between the outgoing pressure and inlet pressure determines the type of compressor that is needed. A compression ratio of more than 2 means that a compressor will be needed. When the compression ratio is lower than 2, a much cheaper blower could be used.

The following data from the equipment design section is required:

- Type of compressor/blower
- Ingoing pressure [bar]
- Outgoing pressure [bar]
- Gas flow rate [m<sup>3</sup>/s]
- Power consumption [Hp]
- Material
- Type of motor (not for a blower)

#### L.1.5.1. Blower

A blower is used in the process where a low compression ratio is present. In the DMC process is one blower present, this is in the first recycle of CO<sub>2</sub>. There are two kinds of blowers; centrifugal or rotary straight-lobe. The latter one has the widest operating range, but is also more expensive.

The general equation to estimate the costs of a blower is given in eq. (L.135).[80]

$$C_P = F_M \left( \frac{I_c}{I_r} \right) C_B \quad (\text{L.135})$$

The material factor is given in Table 95.[80]

Table 95: Material factor for a blower

Material	$F_M$
Cast iron	1.0
Fiberglass	1.8
Stainless Steel	2.5
Nickel alloy	5.0
Aluminum	0.6

The size factor for the price is for both types the same, namely the power consumption in Hp. Where the correlation for a centrifugal blower ((L.136)) is valid between 5 and 1,000 Hp and for a rotary straight-lobe blower ((L.137)) between 1 and 1,000 Hp. CEPCI = 500.[80]

$$C_B = \exp(6.8929 + 0.7900 \ln P_C) \quad (\text{L.136})$$

$$C_B = \exp(7.59176 + 0.79320 \ln P_C - 0.012900(\ln P_C)^2) \quad (\text{L.137})$$

The comparison of the cost equations is given in Figure 132. Only for high power consumptions, the prices of the two types are comparable.

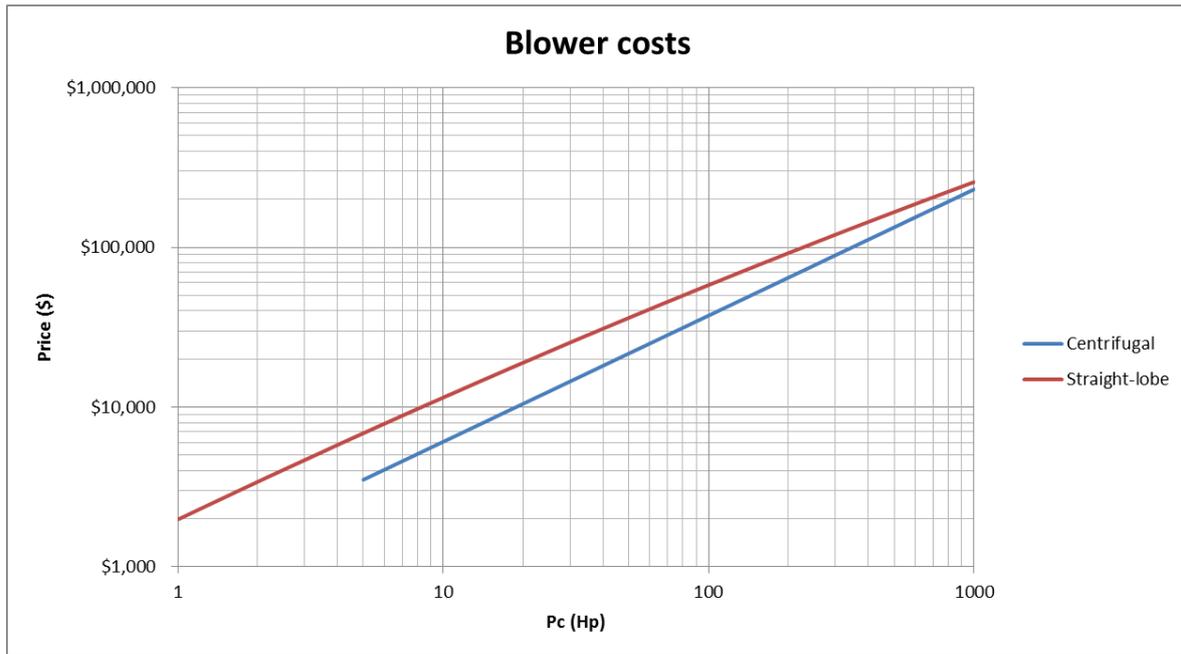


Figure 132: Price comparison of a centrifugal and rotary straight-lobe blower

#### L.1.5.2. Compressor

Compressors are usually account for a large fraction of the total capital expenditure. Three types of compressors are available (centrifugal, reciprocating and screw) and all have different operating ranges as discussed in chapter 9.5. The overall equation for the costs is:[80]

$$C_P = F_D F_M \left( \frac{I_C}{I_r} \right) C_B \quad (L.138)$$

There are correction factors for the material of use and for the driver of the compressor. Usually this is an electric motor, but also gas or steam turbines can be used. The motor drive factors are given in Table 96.[80]

Table 96: Compressor drive factor

Compressor drive	$F_D$
Electric	1.00
Steam turbine	1.15
Gas turbine	1.25

The base case compressor is made of either carbon steel or cast iron. For other materials, the material factor will be larger than one. In case of stainless steel it is 2.5 and 5.0 for nickel-alloy.

For a centrifugal, reciprocating and screw compressor the base costs including the driver is given in equations (L.139) , (L.140) and (L.141) , respectively. The size factor is the power consumption and all equations have different validity ranges. These are respectively between 200 and 30,000 Hp, 100 and 20,000 Hp and 10 and 750 Hp. All have a CEPCI of 500.[80]

$$C_B = \exp(7.5800 + 0.80 \ln(P_C)) \quad (L.139)$$

$$C_B = \exp(7.9661 + 0.80 \ln P_C) \quad (L.140)$$

$$C_B = \exp(8.1238 + 0.7243 \ln P_C) \quad (L.141)$$

With Figure 128, the different compressor types can be compared.



Figure 133: Cost comparison for the different compressor types

#### L.1.5.3. Summary compressor

With these methods, a cost estimation can be made for the compressors present in the process. In Table 97, an overview is given of the final costs, without applying the Lang factor. The total costs for the compressors can be estimated at \$3,000,000,-.

Table 97: Summary of the cost price of the compressors

Number	Type		Gas flow [m <sup>3</sup> /s]	Pin [bar]	Pout [bar]	Power [Hp]	Material	Motor	Price (\$)
CP-2071	Compressor	Centrifugal	4.28	1.00	30.20	4084.20	Carbon steel	Electric	\$ 1,746,988.46
CP-2072	Blower	Centrifugal	0.39	29.80	30.20	31.01	Cast iron	-	\$ 17,111.14
CP-2073	Compressor	Centrifugal	15.80	0.30	1.20	1513.36	Carbon steel	Electric	\$ 789,509.60
CP-2074	Compressor	Centrifugal	0.76	0.80	10.20	392.63	Carbon steel	Electric	\$ 268,281.14
CP-2075	Compressor	Reciprocating	0.05	10.00	30.20	101.40	Carbon steel	Electric	\$ 133,635.29
<b>Total</b>									<b>\$ 2,955,525.63</b>

### L.1.6. Reactor

The reactor is modelled as a heat exchanger with multiple tubes in one shell. Inside the tubes the reaction occurs. Cooling water flows through the shells to cool down the tubes, due to the exothermic reactions.

The design data of the reactor can be found in Table 98.

*Table 98: Input parameters for the economic evaluation*

Parameter	Value	
<b>Length</b>	14.5	m
<b>Diameter of tubes</b>	0.065	m
<b># of tubes</b>	1575	
<b># of shells</b>	8	
<b>Area per shell</b>	582	m <sup>2</sup>
<b>Pressure shell</b>	30	Bar
<b>Material</b>	CS/CS	Shell/tube
<b>Reactor volume</b>	75.8	m <sup>3</sup>

As it is modelled as a heat exchanger the steps taken in this estimation are the same as described in section L.1.1.1 for a shell and tube heat exchanger. Although the reactor is a single pass through the shell, it is assumed to have the same price of a U-tube heat exchanger. For a multi tubular exchanger in one single shell, is no cost price data available.

The tube length correction is not applicable in this case and is therefore taken as 1. Inside the reactor the pressure 30 bar and the cooling water is at approximately 3 bar. For safety reasons, the design pressure of the shell is also taken as 30 bar.

The base price of one shell is given in equation (L.142), with the area in ft<sup>2</sup>. [80]

$$C_B = \exp(11.147 - 0.9186 \ln(A) + 0.0979(\ln A)^2) = \$40,000 \quad (\text{L.142})$$

The design pressure is quite high and the correction factor for the pressure is calculated as: [80]

$$F_P = 0.9803 + 0.018 \left( \frac{P}{100} \right) + 0.0017 \left( \frac{P}{100} \right)^2 = 1.09 \quad (\text{L.143})$$

Carbon steel is used as material of construction for both the shell and the tube, this is the base material. The last correction is for the cost price index. Currently it is at 576 and the correlation is made for a cost price index of 500.

$$C_P = F_P \left( \frac{I_c}{I_r} \right) C_B = \$50,200 \quad (\text{L.144})$$

This is the price for one of the cooling water shells. In total there are 10 shell, 8 for reaction and two for the replacement of catalyst. The total price for the reactor then becomes approximately \$500,000. This is without the Lang factor.

### L.1.7. Summary CAPEX

In this chapter, the capital expenditure of all the equipment is estimated. This is done for heat exchangers (L.1.1), pressure vessels (L.1.2), vessel internals (L.1.3), pumps (L.1.4), compressors (L.1.5) and the reactor (L.1.6). Overall this results in a total investment costs for the plant and that can be calculated with equation (12.1). The Lang factor that will be applied is 6. An overview of the costs of the equipment without applying the Lang factor is given in Table 99.

Table 99: Total CAPEX without Lang factor

Equipment	Costs (M\$)
Heat exchangers	\$ 0.56
Flash vessels	\$ 0.47
Distillation columns	\$ 0.98
Pumps	\$ 0.14
Compressors	\$ 2.96
Reactor	\$ 0.50
<b>Total</b>	<b>\$ 5.60</b>

Filling in equation (12.1) gives:

$$CAPEX = f_L \sum_i C_{pi} = 6 * \$ 5.60 \text{ mln} = \$33,600,000$$

A more schematic overview of the equipment costing is given in Figure 134.

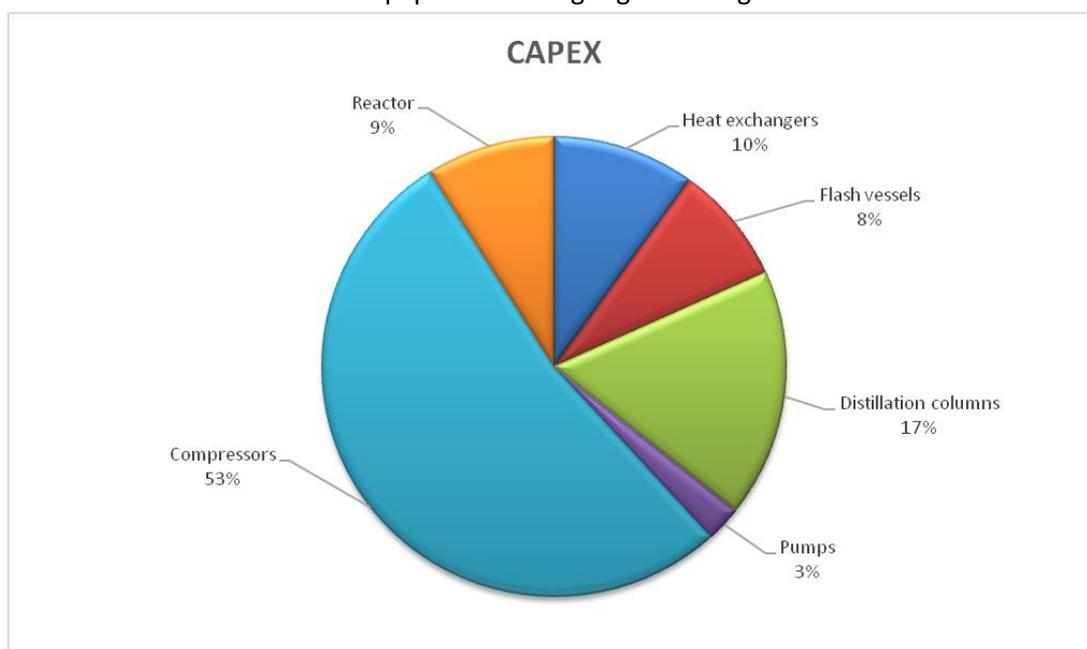


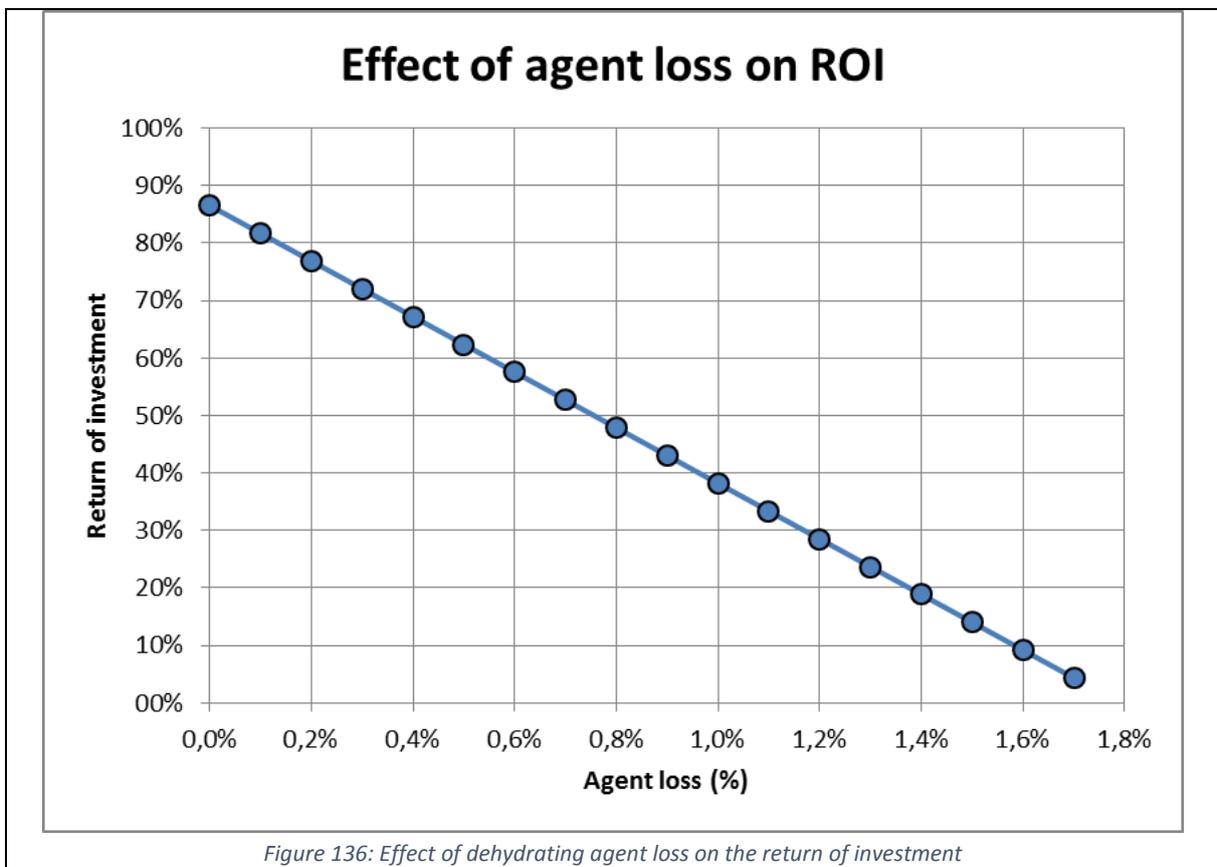
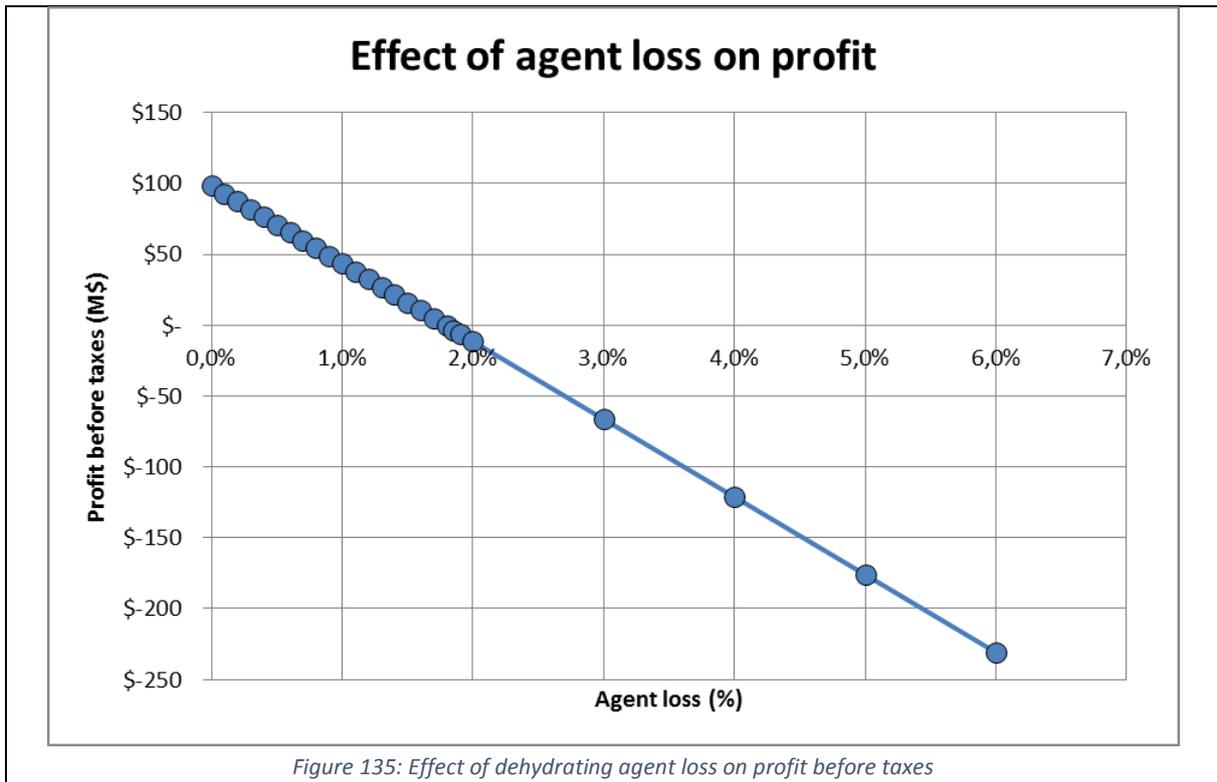
Figure 134: Contributions to the investment of all equipment

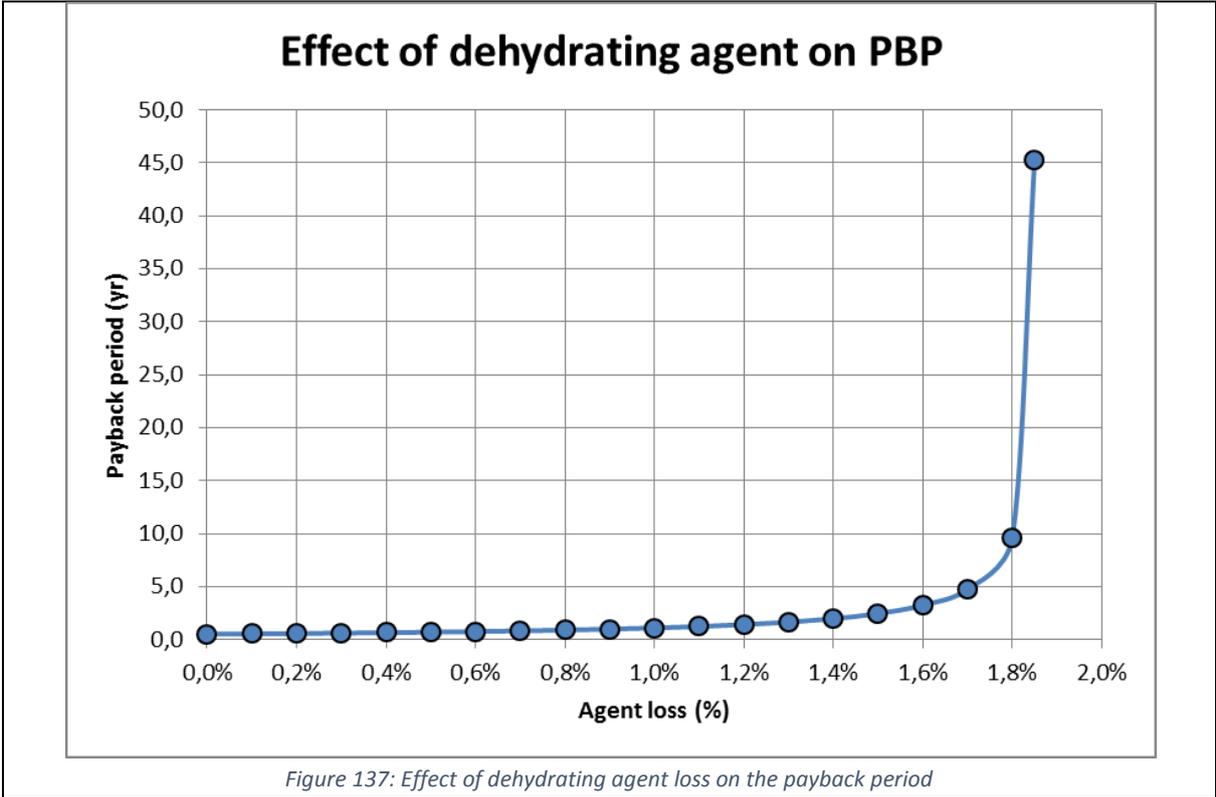
This cost estimation does not include the regeneration part of the process. There is not much known about this part, but it will include a reactor to regenerate the dehydrating agent and afterwards a separation train to obtain a pure 2-cyanopyridine recycle, without losing any 2-cyanopyridine. In chapter 12.3 a sensitivity analysis is made to determine the impact of the investment costs for the regeneration on the economic evaluation.

#### Appendix L.2. Sensitivity analysis

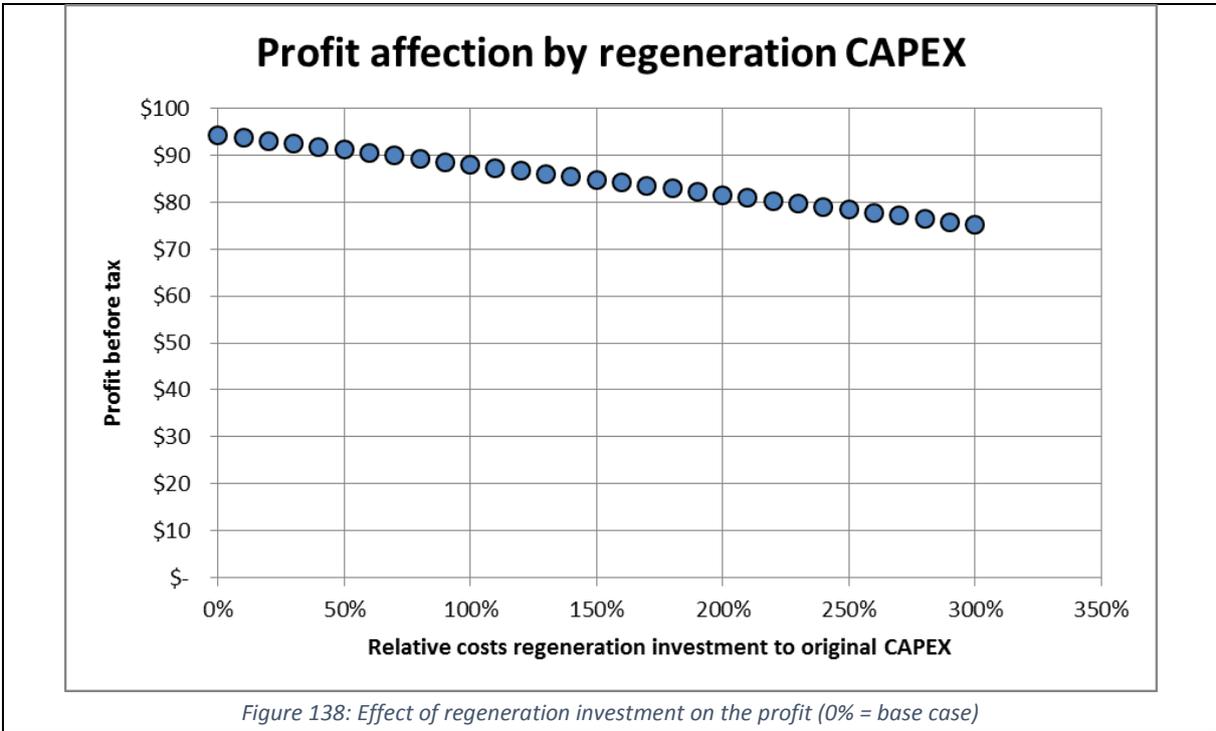
A sensitivity analysis is made for some unknown parameters of the process. These are the loss of dehydrating agent during the process, the investment costs for the regeneration part, frequency of catalyst replacement and methanol price. The latter one is not really an unknown, but the effect of possible fluctuations on the profit is interesting to know. In this Appendix only the graphs resulting from these analyses are shown, the full analysis can be found in chapter 12.3.

L.2.1. Dehydrating agent loss





L.2.2. Regeneration investment



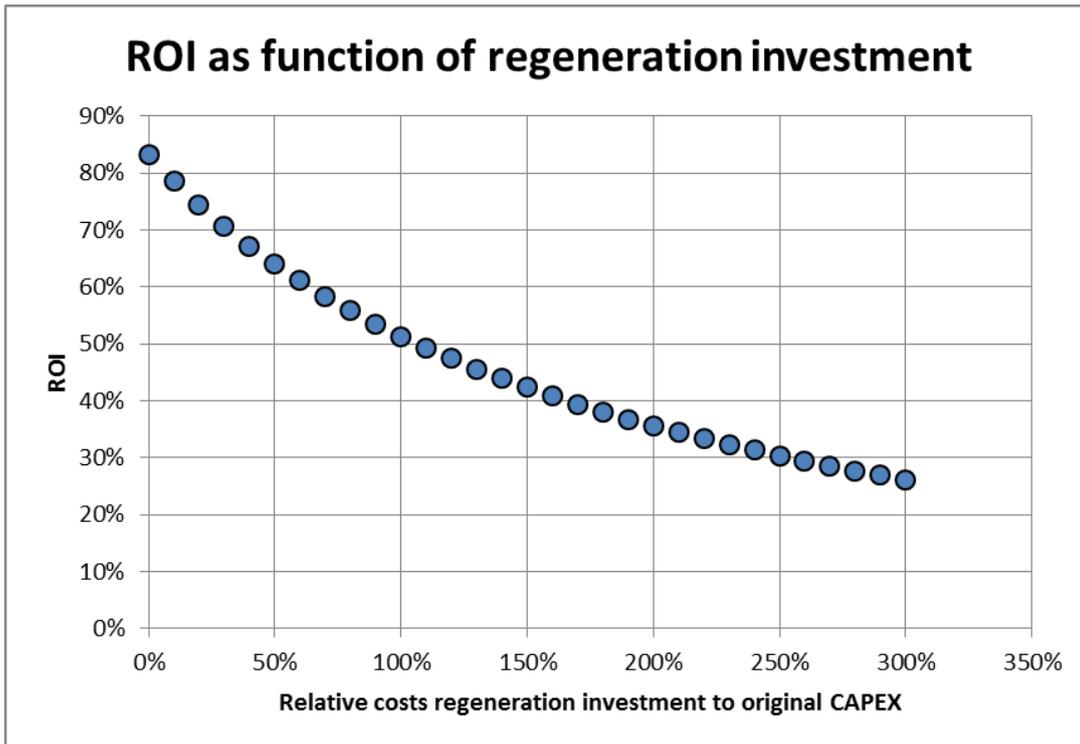


Figure 139: Effect of regeneration investment on the return of investment (0% = base case)

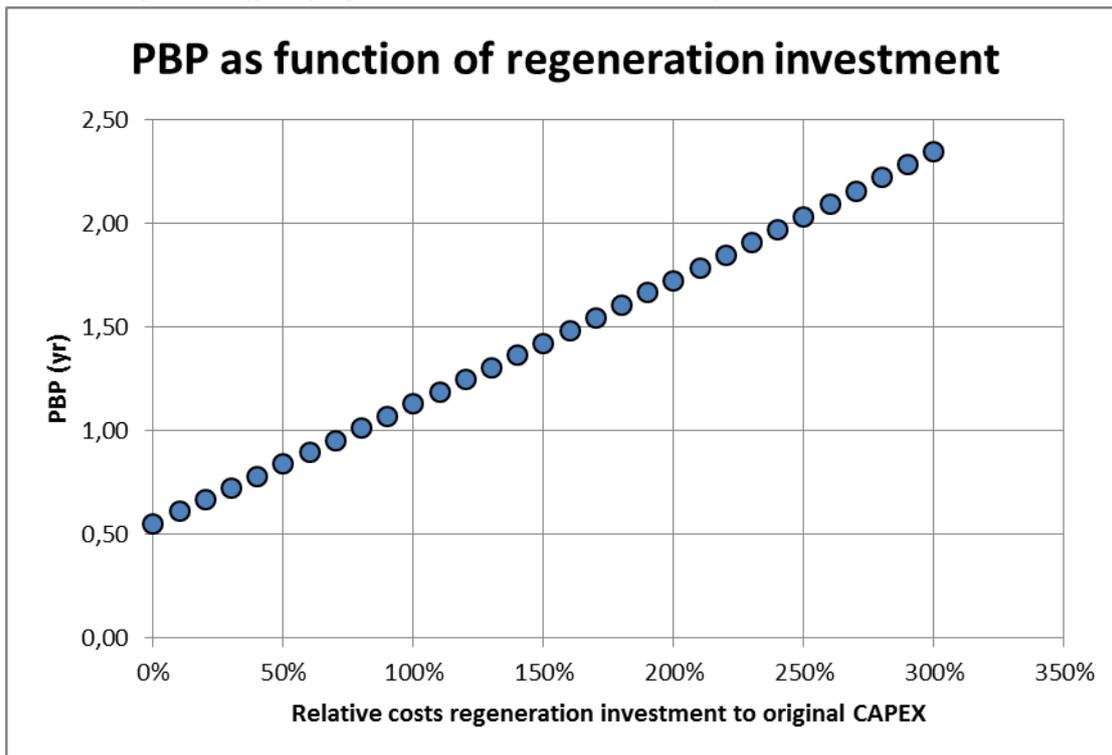


Figure 140: Effect of regeneration investment on payback period (0% = base case)

### L.2.3. Catalyst replacement

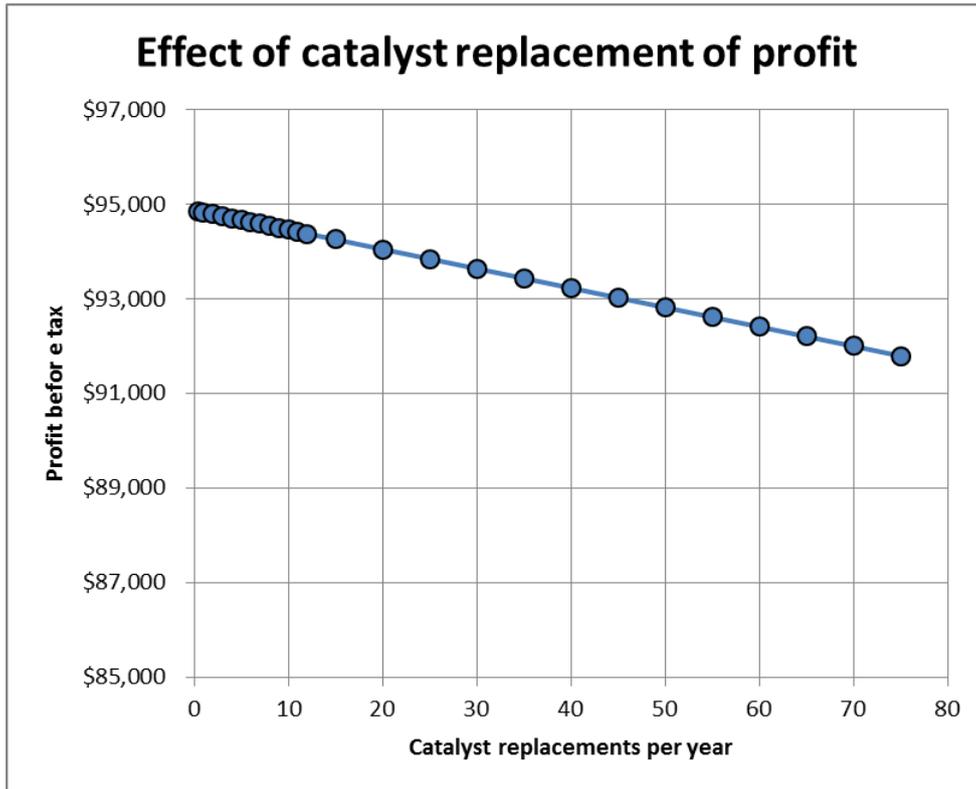


Figure 141: Effect of catalyst replacement on the profit before taxes (12 = base case)

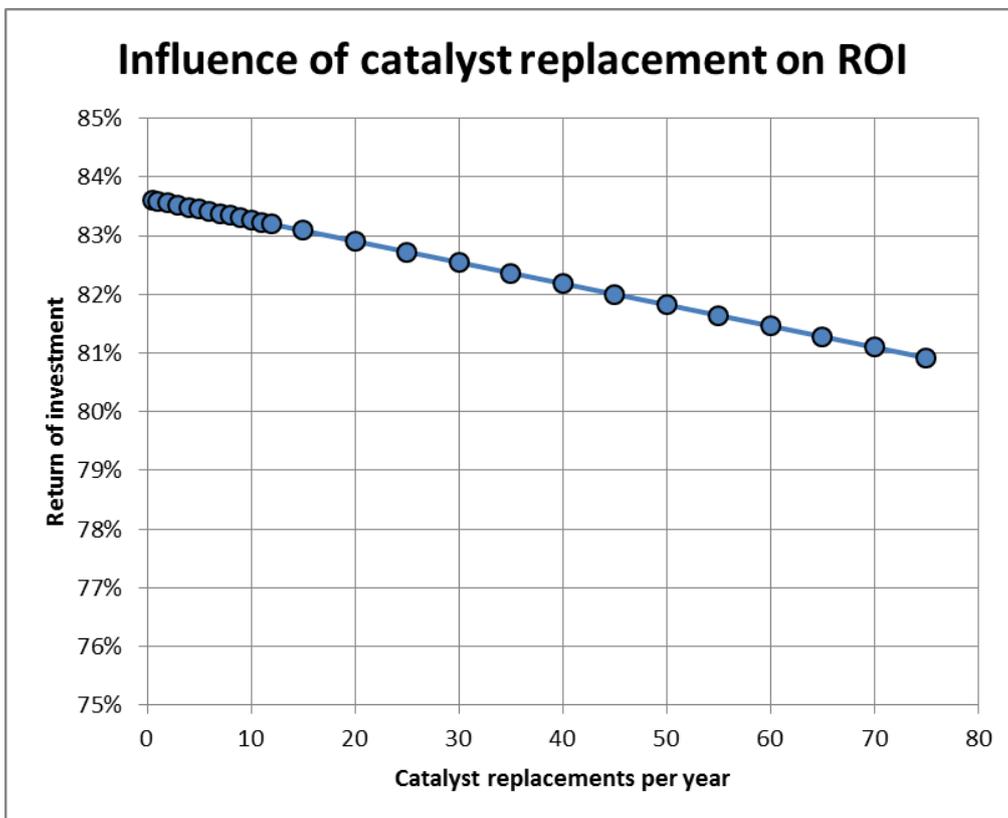


Figure 142: Effect of the frequency of catalyst replacement on the return of investment (12 -base case)

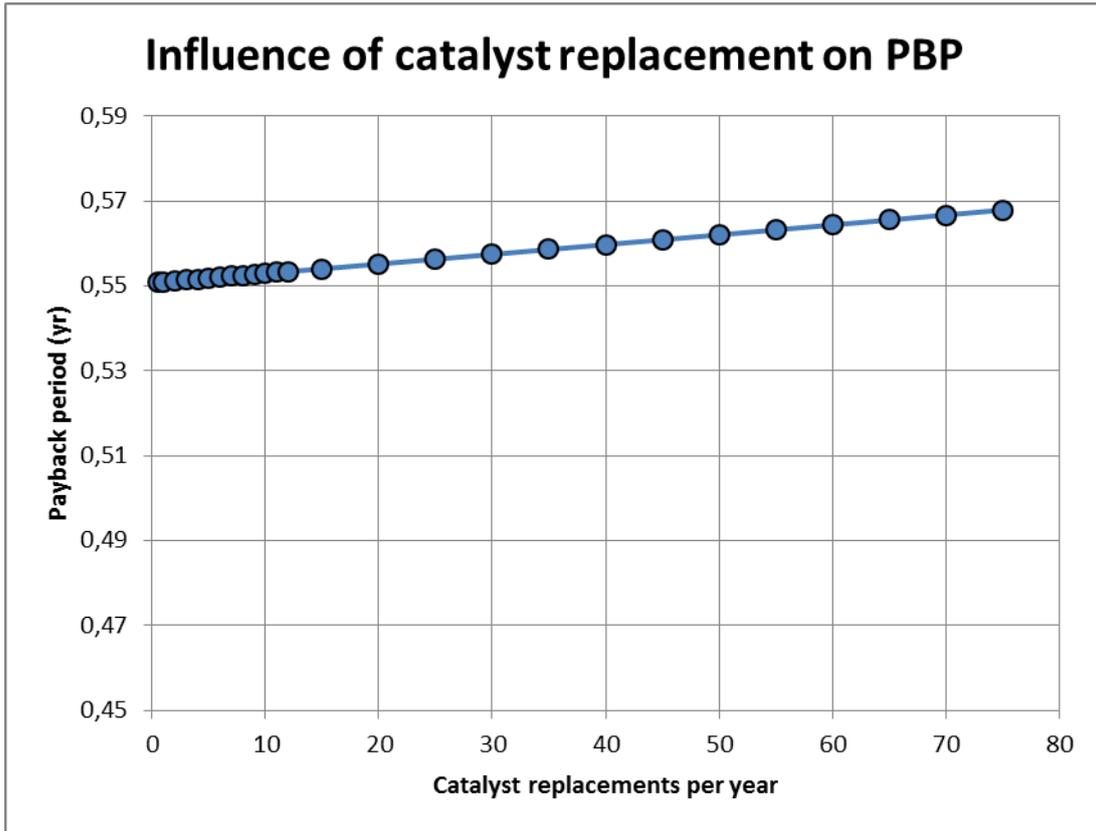


Figure 143: Effect of the frequency of catalyst replacement on the payback period (12 = base case)

#### L.2.4. Methanol price

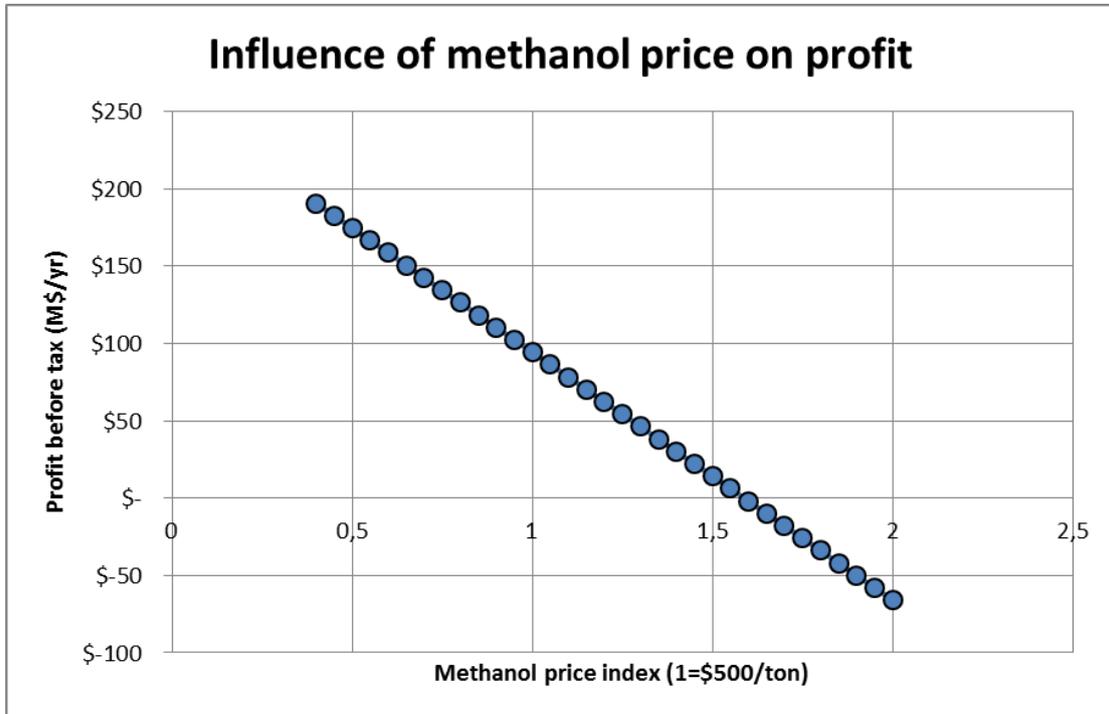


Figure 144: Effect of the methanol price on the profit before taxes (1 = base case)

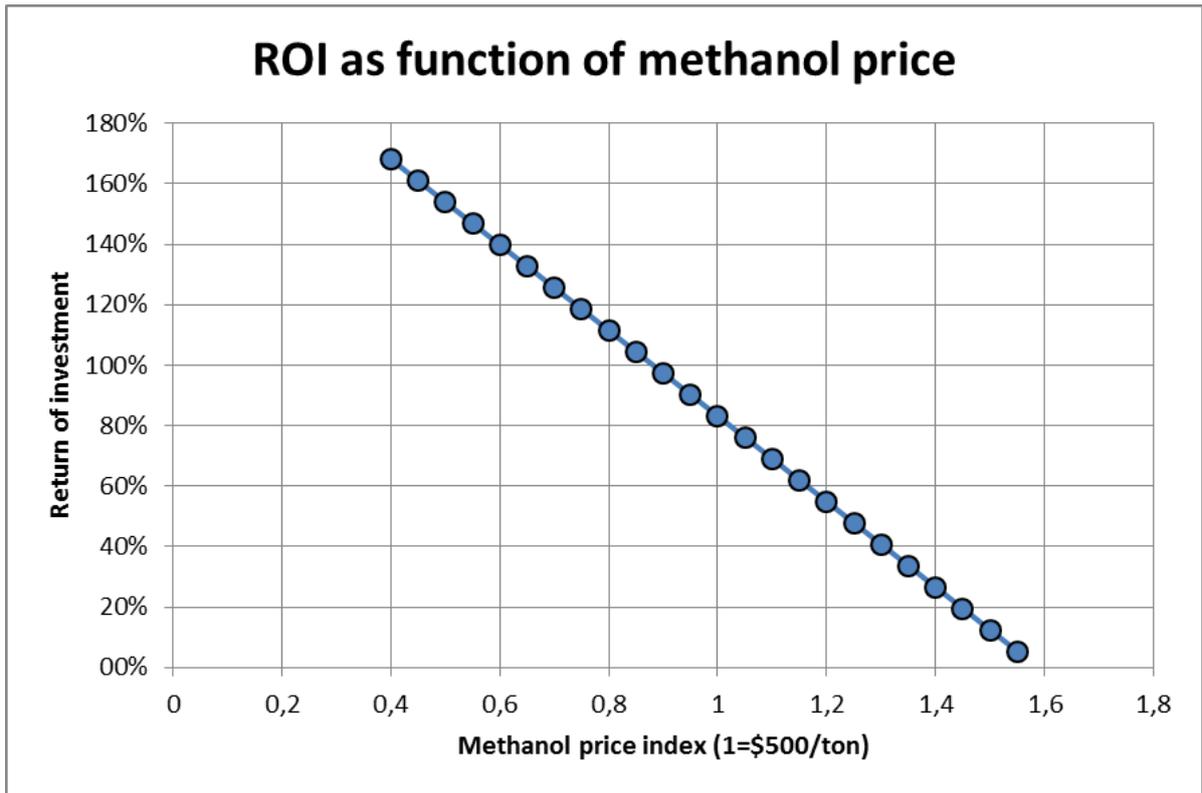


Figure 145: Effect of the methanol price on the return of investment (1 = base case)

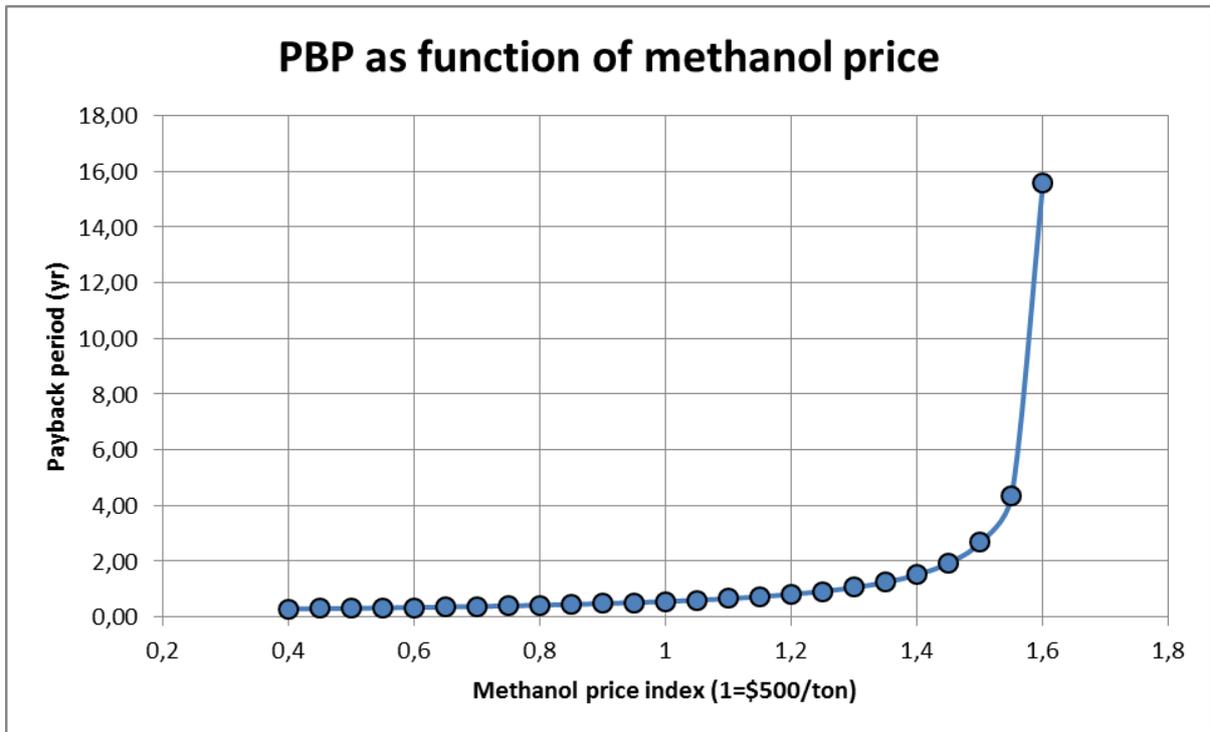


Figure 146: Effect of methanol price on the payback period (1 = base case)