Preliminary Design of a Polyurethane Recycle Plant

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Preface

As a consequence of the increasing environmental pollution a demand for recycling processes has arisen. In order of ICI Rozenburg 6 Mechanical and 4 Chemical engineering students in the final year of their study at The Delft University of Technology have investigated the possibility of a Poly Urethane recycling plant. This report contains the preliminary design of a Polyurethane recycling plant as made during the last three months of 1991.

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Summary

A process for continuous recycling of 1000 kg/h Poly Urethane foam has been designed. The process has been split up in a feed, reaction and a work up section. Unit operations have been designed, and a mass balance has been set up.

The goal of the feed section is to remove water from PU foam blocks and to reduce these blocks into particles of 500 μm solved in MEG. To achieve this 9 possible options have been studied.

Cutting of the blocks takes place in 2 cutters and during the mixing with MEG. In the recommended option the PU is dried by flashing the PU and MEG dispersion. The feed section operates discontinuously. By preparing an hours feed, and storing it, the rest of the process can operate continuously.

Finally the dispersion is heated to 200 °C and pumped to the reactor.

In the reaction section, PU is broken down to a two phase system of flexibles and rigids. The reaction takes place in two equal CSTR's in series with a filter in between. With this configuration, a conversion of 100 % can be guaranteed.

The reactor pressure is 3 bar, the temperature is 200°C. The two phases are separated in a (tube like) settler. Flexibles go to the work up section. MEG is distilled from the rigids phase. A packed and a sieve plate distillation have been designed. The sieve plate distillation has most advantages.

The work-up section removes the excess of MEG and DADPM from the flexible stream, by extraction, flashing and ion-exchange.

A Rotary Disc Contactor, pulsed packed column and a sieve plate column are designed at 80 and 100°C, their costs are calculated and operation and maintenance are discussed. Taking the results of all this in consideration, the RDC extractor is the best solution.

Flashing separates MEG from flexibles and DADPM, a McCabe-Thiele diagram shows that one tray meets the required separation. Design calculations are done for isothermal and adiabatic flashes. The adiabatic flash is preferred, regarding height of vacuum, required heat duty and because it is easier to control.

The ion-exchanger decreases the DADPM fraction in the flexibles to a maximum of 20 ppm. The resin, Amberlyst 15, is used again after regeneration and drying. A 'batch' and 'continuous' process are discussed. The latter, with two columns parallel, is more favourable because of significant lower costs.

Possibly the process will be cheaper if feed section and reactor are combined and operated discontinuously.
1 INTRODUCTION

Poly Urethane (PU) is a well known polymer. It is used in, for instance, car chairs, shoe soles, mattresses and as isolation material.

At the moment waste Poly Urethane is burned, or dumped on garbage belts. Because of a change of attitude towards environmental issues the recycling of this material is gaining interest and it is expected that recycling of waste material has to be done by it’s manufacturer.

That’s why ICI is interested in designing a process for Poly Urethane recycling. Poly Urethane can be chemically split and the products, polyol chains (flexibles) and rigids, can be used again to make new PU.

This report contains the preliminary design of a PU recycle process.

The process is split up in a feed section, for preparation of the solid PU foam for reaction, a reactor section in which the PU is broken down chemically and a workup section for purification of the products. The report is set up the same way. In chapters 5,6 and 7 describing the three sections, several options for unit operations in the plant are discussed and a choices are made. The units operations are linked in chapter 4, resulting in a mass and energy balance and a Process Flow Diagram.
2 ASSIGNMENT DESCRIPTION

The goal of this study is the preliminary design of a plant for the continuous recycling of 1000 kg/h soft Poly Urethane foam. A flowsheet of the plant had to be made, based on a process scheme made by ICI. The mass and energy balance of the complete process had to be determined. All unit operations had to be designed. Special attention had to be paid to the preparation of the feed (an overview of several options for preparation) and the workup of the products.
3 PROCESS SCHEME

3.1 Summary

A process scheme was set up by ICI. Main goal is to break down Poly Urethane to flexibles and rigids, and to remove the harmful side product DADPM. The solvent for the reaction is MEG. The MEG is removed from rigids partly by distillation, and from the flexibles by flashing. DADPM is removed from flexibles by extraction with MEG, followed by ion-exchange. DADPM in the rigids is converted to less harmful components by propoxylation. The propoxylation reactor has not been designed.
3.2 Introduction

The goal is to design a plant for continuous recycling of 1 ton/h Poly-Urethane (PU). This is done by glycolysis of PU with MEG to flexibles (polyol chains) and rigids. MEG is both dispersion agent and reactant. In a side reaction of PU with H₂O, DADPM is formed. DADPM has negative effects on the products, and is poisonous, so it has to be removed and converted to less harmful substances. The H₂O has to be removed as much as possible in advance to avoid the DADPM production. The process scheme is shown in figure 3.1.
3.3 The Process Scheme

The process starts with the preparation of the reaction mixture in the feed section. The main goal of the feed section is to cut PU to small pieces, mix all components for the reaction and to remove H₂O. The PU/MEG ratio is brought to 10 mass %. Water is removed by flashing the reaction mixture at low pressure before it is fed to the reactor. The feed section operates discontinuously. Every hour an hour's feed for the plant is prepared and pumped to a storage vessel. From there the feed is led to the plant continuously.

After being heated to 200°C, the feed enters the reactor system. PU is glycolised with MEG. All PU particles have to be broken down to PU-molecule size to avoid downstream contamination of the plant, this requires a complete conversion of PU. In the side reaction with H₂O, CO₂ is produced. This is vented from the reactor. The reaction products are divided in two liquid phases: a flexibles/MEG phase and a rigids/MEG phase, containing the most of the MEG in the feed. Both phases are contaminated with DADPM, so both have to be purified.

The reactor effluent is led to a settler, where the two phases separate perfectly by gravity. The upper phase is flexibles/MEG, the lower is rigids/MEG.

The lower phase is led to a distillation column, operating at 200°C. The bottom product specification is 5.64 mass % DADPM in the rigids, and a maximum MEG/DADPM ratio of 6. The bottom product goes on to a propoxylation reactor, to convert the DADPM. The propoxylation vessel has not yet been designed. Most of the MEG leaves at the top, the top specification is a maximum of 20 ppm DADPM.

DADPM is removed from the upper layer of the settler (flexibles/MEG) in an extractor, operating at 80°C. The purified flexibles/MEG stream must contain no more than 500 ppm DADPM. The extracting agent is a fraction of the distillation’s top product. The contaminated extracting agent is led back to the distillation column to remove the DADPM.

Because pure flexibles are required as a product, the purified flexibles/MEG stream from the extractor is led to a flash vessel, where a large part of the MEG must be removed, because it contaminates the downstream ion-exchanger. The remaining bottom product (flexibles with little MEG) still contains some DADPM which is removed by the ion-exchanger. The resulting DADPM concentration should be less than 20 ppm.

The MEG vapour from the flash vessel is condensed and combined with the remaining MEG stream from the distillation’s top. The resulting MEG stream, still containing a small amount of DADPM is recycled to the feed section.
3.4 Conclusion

The process scheme has been copied from I.C.I. No extra attention has been given to the scheme. More extensive studies might yield a more efficient process, e.g. by combining the feed section and reactor: so the feed is prepared in the reactor. A continuous production and work up of the products can then be achieved by using several reactors in parallel.
4 MASS BALANCE, ENERGY BALANCE AND PROCESS FLOW DIAGRAM

List of Symbols

A  heat transfer area \([\text{m}^2]\)
c  velocity \([\text{m/s}]\)
Di DADPM flow in stream \(i\) \([\text{kg/h}]\)
F  correction factor [-]
g  acceleration of gravity \([\text{m/s}^2]\)
h  enthalpy \([\text{J/kg}]\)
H  heat exchanger (abbreviation)
M_i MEG flow in stream \(i\) \([\text{kg/h}]\)
P  pump (abbreviation)
P  temperature efficiency [-]
P_{\text{shaft}} shaft work \([\text{kW}]\)
Q  heat load, duty, heat \([\text{J, kW}]\)
R  heat capacity ratio hot/cold stream [-]
U  overall heat transfer coefficient \([\text{W/m}^2 \text{K}]\)
z  height \([\text{m}]\)
\(\Delta T_{\text{Ln}}\) logarithmic temperature difference \([\text{K}]\)
\(\Phi_m\) mass flow \([\text{kg/h}]\)
4.1 Summary

The mass balances of all components in the plant were calculated. MEG and DADPM are recycled (9725 kg/h resp. 0.358 kg/h). A MEG feed of 275 kg/h is required. Other components pass through the plant straight forwardly. Each hour 714 kg flexibles and 351 kg rigids are produced from 1000 kg crude PU.

Knowing all mass flows and the required temperature change of the streams a maximum heat recovery was searched for. The total energy needed for heating is 5356 kW. The heat exchange areas of all the heat exchange equipment are calculated.

Knowing the units in the plant, and the required pressure in flash columns and reactor a pressure profile of the plant was estimated, and pumps were placed where necessary.

The energy required for pumping is 446 kW. The cutters in the feed section require 191 kW, the high shear mixer requires 23 kW.

Mass flows, stream temperatures and pressures and measurements of the unit operations in the plant were put together in a Process Flow Diagram (P.F.D.).

For the stream numbers in this chapter see figure 4.1, these numbers do not correspond with the stream numbers in the P.F.D.
4.2 The Mass Balance

4.2.1 Introduction

From the 'glycolysis flowchart', containing mass flows of glycolysis experiments, an initial mass balance for the process scheme was calculated. The unit operations (see later on in this report) in the plant were designed based on this mass balance and specifications from the flowchart.

MEG containing some DADPM is recycled. The DADPM and the MEG balance of the total plant have to be recalculated, because there was no DADPM recycle in the initial mass balance. Also the performance of the unit operations does not necessarily correspond completely with the initial mass balance. So all performances have to be linked for the calculation of the correct mass balance. This is done with shortcut 'performance equations' of the designed unit operations and simple mass balances.

The following assumptions have been made:

1) separation in the settler is perfect, all flexibles in the top stream, all rigids in the bottom stream,

2) bottom product of the distillation contains all fed rigids and all fed KAc,

3) bottom product of the flash contains all fed flexibles,

4) in flexibles 15 mass % MEG is dissolved,

5) the amount of CO₂ dissolved in the reactor effluent is negligible,

6) only CO₂ and MEG occur in the vapour phase in the reactor.

Assumptions 1 and 4 are given by ICI. Assumptions 2 and 3 are based on the fact that rigids and flexibles are much heavier than MEG, so they will not be present in the top product, this means that there is no recycle of rigids, flexibles, CO₂ and KAc in the plant.

Because only MEG and DADPM are recycled their mass balance has to be recalculated.

4.2.2 The DADPM Balance

An amount of DADPM is recycled (D13 passed on to D1), so the amount leaving the reactor, D3, is equal to the sum of production and recycle, if the balance is correct. The DADPM production is 31.5 Kg/h.
The mass balance is calculated with two kinds of equations: simple equations for mixing/splitting points and units, and 'performance equations' for the units. The equations for the units are:

**settlertime:** \[\frac{\text{DADPM top}}{\text{DADPM bottom}} = 8.5/23\]

**distillation column:** \[\frac{\text{DADPM top}}{\text{DADPM bottom}} = 0.21/30.8869\]

**flash:** \[\frac{\text{DADPM top}}{\text{DADPM bottom}} = 1.31\]

The top/bottom ratio’s result from unit sizing based on the initial mass balance (from the glycolysis flow chart). A constant ratio of top and bottom product can be assumed if the feed of a unit in the resulting mass balance is not much different from the feed the unit was designed for in the first place.

The performance of the extractor was set up based on 4 equilibrium stages.

The mass balance is solved by an iterative process (subscript is iteration number):

\[
\begin{align*}
0) & \quad D_{10} = 0.00 \\
1) & \quad D_{31} = 31.5 \\
2) & \quad D_{131} \text{ results from calculations with MERCURY} \\
3) & \quad D_{11} = D_{131} \\
4) & \quad D_{32} = 31.5 + D_{11} \\
5) & \quad D_{132} \text{ results from calculations with MERCURY} \\
6) & \quad \text{repeat 3,4 and 5 until } D_{3j} = D_{3j+1}
\end{align*}
\]

If 6 is reached, the DADPM balance is solved. The amount of DADPM leaving the reactor is then (exactly) the amount entering plus the amount produced. From calculations an amount of recycled DADPM in 0.358 kg/h results.

The DADPM balance is calculated with the numerical solver MERCURY. The used file is shown in appendix A.4.I.

The results are also shown in A.4.I and the P.F.D. (appendix A.4.III).

### 4.2.3 The MEG Balance

As in the DADPM balance calculations, there are simple mass balances for splitters, mixers and units, as well as 'performance equations' for separation units.

A MEG flow of 10 tones/h enters the plant. MEG is lost in the reactor due to glycolysis and in the streams to propoxylation vessel and ion exchanger. This loss has to be compensated for by adding new MEG from the fresh MEG storage and KAc/MEG storage.

All flexibles go from the settler’s top, to extractor, and all leave at the extractors top. Because there is always 15 % MEG in the flexibles, the amount of MEG from settler to extractor, to flash are readily calculated. The MEG balance across the extractor is straightforward because of the same reason. So \(M_9 = M_8\), and thus \(M_{15} = M_{16}\).
For the distillation column and flash performance equations are used like those in the DADPM balance. These equations are:

- distillation column: \( \frac{\text{MEG top}}{\text{MEG bottom}} = 66.307 \)
- flash vessel: \( \frac{\text{MEG top}}{\text{MEG bottom}} = 184.29 \)

A fresh MEG feed of 275 kg/h is required. The amount of recycled MEG is 9725 kg/h.

The results are shown in appendix A.4.II, and the P.F.D. (appendix A.4.III).

### 4.2.4 Flexibles, Rigids, KAc and CO₂ Balances

Because only MEG and DADPM are recycled, the balance of the remaining components is easily set up. Considering the assumptions made in 4.2.1 the following can be said:

1. all flexibles from the reactor pass the settler's top, go to the extractor and end as the flash bottom product,
2. all rigids and KAc from the reactor pass the settler's bottom, and end as the distillations bottom product,
3. all CO₂ is vented from the reactor.

In an hour 714 kg flexibles and 351 kg rigids are produced from 1000 kg crude PU. The mass flows are shown in the P.F.D. (appendix A.4.III).
4.3 Energetic Considerations

4.3.1 Introduction

An attempt to minimize the energy required for the plant was made. Cold streams are heated with hot streams as much as possible. The remaining required energy can then be calculated.

4.3.2 Heat Recovery

The temperature in the plant does not gradually decrease going down stream. In the reactor and distillation the required temperature is about 200°C, in the extractor 80°C, and in the flash vessel 200°C again. A maximum heat recovery was searched for, by comparing heat load (specific heat*temperature*mass flow) and temperature of streams to be cooled and streams to be heated. A minimum temperature difference of 10°C, required for heat transfer in exchangers, is chosen.

Because the bottom product of the settler goes to distillation carried out at 198°C the settler operation is left at 200°C to avoid unnecessary cooling of the reactor effluent and heating of the settler effluent. Such a temperature will not influence the performance of the settler negatively. The top product of the settler going to the extractor has to be cooled (see later on).

In the feed section MEG from storage (35°C) must be heated to 150°C to perform the flash for dehydration of the feed, and after that heated to 200°C for reactor conditions. The heat required is taken partly from the recycle MEG stream (13). By doing this the feed is prepared for flash and reaction, and the recycled MEG is cooled down to storage temperature.

The vapour stream at the distillation’s top has a large heat load (due to the latent heat of MEG) compared to the other streams in the plant. The latent heat can not be used directly to reboil the bottom product, because condensation and reboiling occur at the same temperature (198°C). The condensating stream can be used elsewhere on site f.i. for generation of steam. For the reboiling steam, or an other heating medium, will have to be used.

The performance of the extractor gets worse at higher temperatures, so the 80°C mentioned above must be maintained. This means that extractor feed streams (15 and 8) must be cooled, product stream 9 must be heated and vaporised for the conditions required in the flash vessel, and 16 must be heated before entering the distillation column. Heat is recovered by cooling the extractor feeds with the extractor product streams.

Before entering the ion-exchanger, the flash bottom product (11) must be cooled to 120°C to avoid damage of the ion-exchangers packing. Because the heat load of this
stream is insufficient to be used for heating else where in the plant, it is cooled with cooling water.

As mentioned a minimum temperature difference of 10°C is needed for heat transfer. So a cold stream at e.g. 80°C can be heated to a maximum of 190°C, if the hot stream is 200°C. On the other hand a hot stream at 200°C can be cooled to a minimum of 90°C with a cold stream of 80°C. The above means that additional coolers and heaters are needed in the plant. For cooling water is used, the heating agent is steam. The exchangers, coolers and heaters to be placed are shown in the P.F.D. (appendix A.4.III)

4.3.3 Heat Transfer Equipment and Stream Temperatures

All heat transfer equipment has been designed except the distillation’s condensor and reboiler.

The heat transfer area of each exchanger has been calculated according to van den Bergh [1]:

\[ Q = U A \Delta T_{Ln} \]  \hspace{1cm} (4.1)

in which: \( Q = \) heat to be transferred  
\( U = \) overall heat transfer coefficient  
\( A = \) required heat transfer area  
\( \Delta T_{Ln} = \) mean logarithmic temperature difference

\[ \Delta T_{Ln} = \frac{\Delta T_{max} - \Delta T_{min}}{\ln(\frac{\Delta T_{max}}{\Delta T_{min}})} \]  \hspace{1cm} (4.2)

\[ \Delta T_{max} = T_{hot,in} - T_{cold,out} \]
\[ \Delta T_{min} = T_{hot,out} - T_{cold,in} \]

If the streams in the exchanger are not completely counter current, equation 4.1 has to be modified:

\[ Q = U A \Delta T \]
\[ \Delta T = F(P,R) \Delta T_{Ln} \]  \hspace{1cm} (4.3)

The constants \( P \) (or \( S \)) and \( R \), and thus the correction factor \( F \), are a function of the temperatures of feed and product streams of an exchanger.

By choosing a temperature drop and raise \( P \) and \( R \) are determined. The factor \( F \) must the be read from figures with curves linking \( P,R \) and \( F \). There are figures for different numbers of shell and tube passes. As for certain \( P \) and \( R \) only one of these figures yields an \( F \), the required number of shell passes is known.

Appropriate values of \( U \) are chosen from Coulson and Richardson [2].
<table>
<thead>
<tr>
<th>HEAT EXCHANGER</th>
<th>HOT/COLD STREAM</th>
<th>TEMPERATURE (°C)</th>
<th>DUTY (k Watt)</th>
<th>A (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁</td>
<td>MEG</td>
<td>170 → 46</td>
<td>924.2</td>
<td>385.17</td>
</tr>
<tr>
<td></td>
<td>MEG,PU,KAc</td>
<td>150 → 35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>MEG,H₂O</td>
<td>139 → 139</td>
<td>70.6</td>
<td>1.083</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>40 → 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₃</td>
<td>MEG</td>
<td>198 → 170</td>
<td>235.7</td>
<td>37.258</td>
</tr>
<tr>
<td></td>
<td>MEG,PU,KAc</td>
<td>163.7 → 139</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₄</td>
<td>steam</td>
<td>250 → 200</td>
<td>349.2</td>
<td>13.196</td>
</tr>
<tr>
<td></td>
<td>MEG,PU,KAc</td>
<td>200 → 163</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₅</td>
<td>CO₂,MEG</td>
<td>200 → 200</td>
<td>22.49</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>40 → 30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₆</td>
<td>MEG/DADPM</td>
<td>198</td>
<td>4596</td>
<td></td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>steam-generation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₇</td>
<td>steam</td>
<td>reboiling</td>
<td>4625</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MEG/DADPM</td>
<td>198</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>/rigids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₈</td>
<td>MEG,DADPM</td>
<td>90 → 80</td>
<td>6.189</td>
<td>0.203</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>27 → 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₉</td>
<td>MEG,DADPM</td>
<td>198 → 90</td>
<td>73.8</td>
<td>32.84</td>
</tr>
<tr>
<td></td>
<td>MEG,DADPM</td>
<td>180 → 80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₁₀</td>
<td>Flex,DADPM</td>
<td>90 → 80</td>
<td>5.096</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>40 → 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₁₁</td>
<td>MEG</td>
<td>198 → 198</td>
<td>29.88</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>40 → 35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₁₂</td>
<td>Flex,DADPM</td>
<td>200 → 90</td>
<td>60.26</td>
<td>38.65</td>
</tr>
<tr>
<td></td>
<td>Flex,DADPM</td>
<td>191 → 80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₁₃</td>
<td>steam</td>
<td>210 → 200</td>
<td>32.83</td>
<td>4.306</td>
</tr>
<tr>
<td></td>
<td>Flex,DADPM</td>
<td>198 → 191</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₁₄</td>
<td>Flex,DADPM</td>
<td>200 → 120</td>
<td>35.55</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>40 → 20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

table 4.1 Heat transfer equipment, and resulting stream temperatures
Calculations concerning the exchangers are not expanded on here, but a summary is given in table 4.1. and 4.2. The exchanger numbers correspond with those in the P.F.D.. An example of exchanger 'design' for H9 is shown if appendix A.4.IV.

4.3.4 The Energy Balance

The energy balance of a steady state flow process is given by:

\[ Q = \Phi_m [(h_2 - h_1) + \frac{1}{2} (c_2^2 - c_1^2) + g (z_2 - z_1)] + P_{shaft} \]  \hspace{1cm} (4.4)

in which

- \( \Phi_m \): mass flow in kg/s
- \( Q \): heat supplied to the system in J/s
- \( h \): enthalpy in J/kg
- \( c \): velocity in m/s
- \( g \): acceleration of gravity in m/s^2
- \( z \): elevation in m
- \( P_{shaft} \): shaft work done by the system in J/s

In this stadium of designing the kinetic and potential energy are neglected.

The energy balance then reduces to:

\[ Q = \Phi_m [(h_2 - h_1)] + P_{shaft} \]  \hspace{1cm} (4.5)

In this global calculation the whole plant is supposed to operate adiabatic i.e. no heat is transferred from or to the surroundings. Energy is only added or taken from the system by heat exchangers. There are no other heat effects in the plant. The reaction enthalpy is negligible.

The total heat supplied to the plant (\( Q \)) can then be found by adding all heat transferred by the heat exchangers, coolers, etc. To compute these individual heat transfers the energy balance was made for each heat transfer unit. This energy balance is given by

\[ Q = \Phi_m (h_2 - h_1) \]  \hspace{1cm} (4.6)

as there is no shaft work done in an exchanger. The results are shown in table 4.2.

The total shaft work done by the plant (\( P_{shaft} \)) can be found by adding all work done by the pumps and the cutters. The pump duties are shown in table 4.3.

Finally the enthalpy difference between reactants (i.e. 1000 kg/h PU and MEG 10000 kg/h) and products (i.e. 714 kg/h flexibles, 351 kg/h Rigid, 31.5 kg/h DADPM and 9884 kg/h MEG) should be calculated. This is not done here because it is not easy to calculate the enthalpy of, for example, solid PU foam and because these three results would not obey the second equation.
<table>
<thead>
<tr>
<th>unit No</th>
<th>Device</th>
<th>Duty (kW)</th>
<th>number of shell passes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>heat exchanger</td>
<td>+924.2</td>
<td>6</td>
</tr>
<tr>
<td>H3</td>
<td>heat exchanger</td>
<td>+235.7</td>
<td>2</td>
</tr>
<tr>
<td>H9</td>
<td>heat exchanger</td>
<td>+73.8</td>
<td>6</td>
</tr>
<tr>
<td>H12</td>
<td>heat exchanger</td>
<td>+60.3</td>
<td>5</td>
</tr>
<tr>
<td>H4</td>
<td>heater</td>
<td>+349.2</td>
<td>1</td>
</tr>
<tr>
<td>H7</td>
<td>heater/reboiler</td>
<td>+4625.0</td>
<td>-</td>
</tr>
<tr>
<td>H13</td>
<td>heater</td>
<td>+32.8</td>
<td>2</td>
</tr>
<tr>
<td>H5</td>
<td>condensor</td>
<td>-2.3</td>
<td>1</td>
</tr>
<tr>
<td>H6</td>
<td>condensor/distillation</td>
<td>-4596.0</td>
<td>-</td>
</tr>
<tr>
<td>H11</td>
<td>condensor</td>
<td>-29.9</td>
<td>1</td>
</tr>
<tr>
<td>H14</td>
<td>cooler</td>
<td>-35.6</td>
<td>1</td>
</tr>
<tr>
<td>H8</td>
<td>cooler</td>
<td>-6.2</td>
<td>1</td>
</tr>
<tr>
<td>H10</td>
<td>cooler</td>
<td>-5.1</td>
<td>1</td>
</tr>
</tbody>
</table>

table 4.2. Heat transfer equipment duties and operation
The reason for this is that we assumed, among others, pressure fall in the piping and this would result in heating up the fluid or heat loss to the surroundings.

However from the tables it can be read how much heat and electrical power is required for the process.

The heat required is calculated by adding the duties of all heaters (H7,H13,H5): 5356 KW. Note that a great deal of energy can be recovered by e.g. generating steam with the distillation's condensor (H6).

The pump work can be calculated from table 4.3. For each pump the volume flow is known, and a pressure raise required is estimated by assuming a 0.3 bar pressure drop across each heat exchanger shell. With this information the required duty of each pump can be calculated. Because pump 1 only operates 7.5 minutes in an hour it's duty has to be multiplied by (7.5/60). The total energy for pumping is then: 446 kW.

The high shear mixer requires 30 kW. Because it operates 45 minutes an hour it's 'time average duty' is (45/60)*30=23 kW.

The duties of the cutters is high: cutter 1, 40.5 kW and cutter 2, 150 kW.

The total work (cutters, high shear mixer and pumps) is: 700 kW.
<table>
<thead>
<tr>
<th>Pump number</th>
<th>Duty (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3500</td>
</tr>
<tr>
<td>2</td>
<td>0.950</td>
</tr>
<tr>
<td>3</td>
<td>0.026</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>2.3</td>
</tr>
<tr>
<td>6</td>
<td>0.230</td>
</tr>
<tr>
<td>7</td>
<td>0.020</td>
</tr>
<tr>
<td>8</td>
<td>1.2</td>
</tr>
<tr>
<td>9</td>
<td>0.016</td>
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<tr>
<td>10</td>
<td>0.082</td>
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<td>11</td>
<td>0.078</td>
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<tr>
<td>12</td>
<td>0.095</td>
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<tr>
<td>13</td>
<td>0.050</td>
</tr>
<tr>
<td>14</td>
<td>3.5</td>
</tr>
<tr>
<td>15</td>
<td>0.015</td>
</tr>
</tbody>
</table>

table 4.3. Pump summary.
4.4 The Process Flow Diagram

The streams from the mass balance were determined and used to calculate the performance of the heat exchangers. The temperatures of the resulting streams were set or calculated simultaneously. The temperature profile of the plant is therefore known.

The pressure in the plant has a given value in certain units:

1 flash in feed section: 0.15 bar
2 reactors: 3 bar
3 flash for flexibles/MEG separation 0.10 bar

The pressure in the reactor is used to push the effluent to the settler. A pressure loss of 1 bar is assumed so the settlers operating pressure is 2 bar.

Assuming a pressure drop of 0.3 bar's for an exchanger shell the pressure in the extractor becomes about 1 bar. Pumps are needed to transport the extractor's effluent through heat exchangers to the flash and the distillation column.

The vacuum in the flash is accomplished by a pump for the bottom product and the condensation of the top product. The condensate must be pumped to the crude MEG storage, again across heat exchangers.

An estimation of the pressure profile has been made, the result is shown in the P.F.D. (appendix A.4.III).

Measures and duties of relevant units in the plant are all shown on the P.F.D.
4.5 Conclusion

The mass balance set up in this chapter will be quite accurate. For rigorous calculations a flow-sheet program like Chemcad, Process or Aspen can be used. This has not been done here because of lack of time to get fully acquainted with such a program.

The heat recovery scheme has been set up by trial, to find an optimum in heat recovery. By using pinch technology, a more optimal recovery might be found. It is not expected that improvements will be large because this recovery scheme was the best of several options for recovery that have been tried.

The design of the units is discussed further on in this report. Design of the heat transfer equipment has been superficial. It goes without saying that more extensive design is required. This can be done with the aid of, for instance, Hextran: a heat exchanger design program.

As the exchangers must be designed extensively, and the heat recovery might be improved the temperature profile of the plant may change. But still the temperatures in reactor, extractor and flash vessels are set, so no major changes are expected.

The pressure profile of the plant has been estimated roughly, no pressure losses in piping or in the unit operations have been regarded. More rigorous calculations can also be done with Chemcad, Process or Aspen. This results in different duties of the pumps.
Literature


5 FEED SECTION

List of Symbols

- $A_{pec}$: Specific area [m²/m³]
- $c$: Concentration of water [kg/m³]
- $c^*$: Concentration of water at the interface [kg/m³]
- $c_0$: Concentration of water in the incoming gas-flow [kg/m³]
- $c_p$: Heat capacity [KJ/molK]
- $D$: Diffusivity coefficient [m²/s]
- $d_b$: Bubble diameter [m]
- $E_{oc}$: Column efficiency [-]
- $F$: Feed flow [mol/s]
- $G$: Gasflow [mol/s]
- $H$: Enthalpy [KJ/mol]
- $H_e$: Henry constant [Pa]
- $K$: Molar distribution coefficient [-]
- $K_l$: Mass transfer coefficient gas-liquid system [m/s]
- $k_g$: Mass transfer coefficient gas-solid system [m/s]
- $L$: Liquid flow [mol/s]
- $M$: Molecular mass [kg/mol]
- $m$: Volumetric distribution coefficient [-]
- $P$: Pressure [Pa]
- $p_{vap}$: Vapour pressure [Pa]
- $R$: Gas constant [J/molK]
- $S$: Surface area [m²]
- $s_{new}$: Surface renewal rate [1/s]
- $T$: Temperature [K]
- $u$: Gas velocity [m/s]
- $V$: Volume [m³]
- $W$: Width of the bed
- $x$: Mole fraction in gas phase [mol/mol]
- $x_m$: Mass fraction in solid phase [kg/kg]
- $x_v$: Volume fraction in solid phase [m³/m³]
- $y$: Mole fraction in liquid phase [mol/mol]
- $z$: Mole fraction in the feed [mol/mol]

Greek symbols

- $\gamma$: Activity coefficient of water in MEG [-]
- $\Delta$: Film thickness [m]
- $\varepsilon$: Volume fraction [-]
- $\Theta$: Contact time [s]
- $\rho$: Density [kg/m³]
- $\Phi$: Molar flux [mol/s]
\( \phi \) mass flux \([\text{kg/s}]\).
\( \phi_v \) gas flow \([\text{m}^3/\text{s}]\).

Subscripts

bed Dryer bed
meg Mono ethylene glycol
N\(_2\) Nitrogen
l liquid phase
g gas phase
tot total
wm water in MEG system
film according to the Film model.
higbie according to the Higbie model.
danckwert according to the Danckwert model
H\(_2\)O water.
PU Poly-urethane foam.
i input.
u output.
s solvent
solid solid phase.
5.1 Summary

The goal of the feed section of the Poly Urethane Recycling Plant is to produce a 200°C dispersion of PU and MEG in a 1:10 ratio out of 1000 kg/h crude PU. The only reason why a 1:10 dispersion is made is that this mixture is pumpable. The three main problems that have to be solved are:

- Reduction of the crude PU size to particles with a diameter $< 500 \text{ mm}$.
- Removal of moisture out of the PU foam.
- Mixing of the PU with MEG.
- Degassing of the PU.

Nine options to reach this goal have been investigated. Only one option is feasible.

Reduction of PU size takes place in two consecutive steps. First the particle size is reduced to a 10 mm diameter in regular granulators. Because of the structure of PU foam further size reduction in these granulators is not possible. Heat generation by friction will lead to decomposition of the PU. The final size reduction takes place after mixing with MEG in a high shear mixer.

Production of the dispersion takes place in a mixing/cutting vessel. First the vessel is filled with MEG. The PU particles are added until the desired ratio (1:10) is reached. The PU is added continuously to avoid blockage of the high shear mixer by un-cut particles and absorption of the MEG by the PU.

The crude PU contains 1.0 mass % of H$_2$O. H$_2$O leads to formation of DADPM in the reactor. Therefore as much moisture as possible has to be removed. Due to the low initial moisture content regular dryers can hardly be used. Out of nine drying options investigated the best way to remove moisture from the PU is by adiabatically flashing the dispersion at a temperature of 150°C and pressure of 0.1 bar. 83.8 % of the moisture is removed from the dispersion.

In the high shear mixer the cavities in the PU foam are destroyed. The gas escapes and is pumped away at the top of the mixing vessel.

Finally the dispersion is heated to 200°C and pumped to the reactor.

It has to be said that almost all calculations are base on theory solely. Hardly any experimental data on PU behaviour are available.
5.2 Introduction

The primary goal of the feed is to deliver a continuous flow of a 1:10 dispersion of PU and MEG to the reactor with a temperature of 200°C. In this chapter 9 methods are investigated to reach this goal. To get an overall view of the options the diagram in Appendix A5.I is used.

This chapter is built up chronologically. In 5.3 is dealt with the storages for PU, MEG and KAc.
All options use the same PU cutting principle and 8 out of 9 use the same mixing technique. To avoid explaining the operation of these machines again with every option in 5.4 is dealt with cutters 1 and 2 and the mixing/cutting vessel.

In 5.5 all drying options are being investigated. First is generally explained how the option works. Then calculations on performance are made. Almost all calculations are based on theoretical models since hardly any practical information is present about cutting and drying behaviour of PU. Every option is finished with a summation of advantages and disadvantages.

In 5.6 the best option is selected. This option is also printed in the P.F.D.
5.3 Storage Tanks

At the beginning of the process 4 storage tanks are needed (See PFD):

- Crude MEG tank
- MEG tank
- MEG with KAC tank
- PU storage

The liquids are not corrosive so carbon steel can be used for all the tanks. A normal relation between the height and the diameter of the tank is: $H/d=1.3$ and it is normal to fill a tank for 80%. The massflow is 10,000 kg MEG per hour with a density of 1100 kg/m$^3$ this is about 10 m$^3$ MEG per hour. A tanker contains about 30 m$^3$ and this data is used to choose the volumes of the tanks. A storage of 30 m$^3$ means a storage for 3 hours.

Every hour 20 kg KAC which is mixed in MEG (ratio 1:1) is needed. 20 kg of MEG with 20 kg KAC is about 0.02 m$^3$. A storage of 0.06 m$^3$ is also a storage for 3 hours.

Calculations for the dimensions of each tank are as follows:

- Crude MEG and MEG tank:

$$V = 0.8 \frac{\pi D^2 H}{4} = 0.8 \frac{1.3 \pi D^3}{4} = 30$$

This gives: $D = 3.32$ m, $H = 1.3 \times D = 4.32$ m and $V_{tank} = 37.5$ m$^3$.

- MEG with KAC tank:

$$V = 0.8 \frac{\pi D^2 H}{4} = 0.8 \frac{1.3 \pi D^3}{4} = 0.06$$

This gives: $D = 0.42$ m, $H = 1.3 \times D = 0.54$ m and $V_{tank} = 0.075$ m$^3$.

- Storage tank before reactor:

$$V = 0.8 \frac{\pi D^2 H}{4} = 0.8 \frac{1.3 \pi D^3}{4} = 20$$

This gives: $D = 2.9$ m, $H = 1.3 \times D = 3.8$ m and $V_{tank} = 25$ m$^3$.

For cost calculations is referred to Appendix A5.XVII.
<table>
<thead>
<tr>
<th>Cutter</th>
<th>Input diameter</th>
<th>Output diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Foam blocks</td>
<td>5 cm</td>
</tr>
<tr>
<td>2</td>
<td>5 cm</td>
<td>1 cm</td>
</tr>
<tr>
<td>3</td>
<td>1 cm</td>
<td>500 μm</td>
</tr>
</tbody>
</table>

Table 5.1: PU Particle Size Reduction Steps

Figure 5.1A: Cutter 1 (UNTHA)

Figure 5.2: Sieve Plate (UNTHA)
5.4 The Making of Small Particles

In this chapter will be described how big foam blocks can be made into smaller parts. On demand of the reactor section PU particles must have diameter of about 500 μm when they leave the feed section. It is possible to make particles with a minimum diameter of 1 cm by regular cutting the blocks. Unfortunately it is impossible to cut the blocks into a diameter smaller than 1 cm because too much heat will be released in the cutter. This leads to degradation of the PU foam. A minor disadvantage is that the cutting process will take a lot of time.

The best way to reduce the blocks into particles of 1 cm is to have two machines connected in series. The first one cuts the PU blocks in manageable pieces of about 5 cm diameter and the second one cuts these pieces into pieces of 1 cm. This construction makes it possible to realize a massflow of 1000 kg PU foam per hour.

After cutting the particles are entered into a vessel with mono ethylene glycol (MEG) as solvent. In the vessel a high speed mixer induces very high shear stresses on the particles. The shear stresses tear the particles apart into very small pieces (500μm). After the feed section the PU particles, dissolved in MEG, are pumped to the reactor.

All the 9 feed options as described in this chapter use the same pre-cutters. Besides that, 8 out of 9 options use the same mixing/cutting vessel. In Table 5.1 a short scheme is presented of the subsequent size reduction steps. Each step is carried out by a separate machine. These machines, cutters 1 & 2 and the mixing/cutting vessel will be described in the next section.

5.4.1 Cutter 1

The first cutter has to reduce the foam blocks into manageable pieces with a size of about 5 cm. Because of its place in the process this machine is called a pre-cutter. The foam blocks are thrown in a hopper above the cutter (See Figure 5.1 & 5.2). Rotating knives in the machine will continuously pull the blocks out of the hopper into the cutter. At the bottom of the cutter a sieve plate with holes of 5 cm diameter is installed. This plate keeps pieces bigger than this diameter from leaving the cutter. Each foam particle is cut over and over again until the size is small enough to pass the sieve plate. Cutters that can handle 1000 kg/h are successfully being used by Agglorex S.A. Belgium. For more information on cutter manufacturers and users is referred to Appendix A5.XXIII.

Price: The price of this type of cutter is about:Hfl. 150,000.--.
Figure 5.3: Cutting Part of Cutter 2 (Mica Machinery).
5.4.2 Cutter 2

The second machine has to reduce the particle size from 5 to 1 cm. The pieces of 5 cm are thrown out of the first cutter on a conveyor. The conveyor transports the pieces to the second cutter. The second cutter differs little from the first one. The first difference is that the knives are replaced for pins (see Figure 5.3). The second difference is the output mechanism. The PU particles are blown out of the cutter by a blower. Features of the machine shown in Figure 5.3 are:

- The machine is equipped with an integral fan which blows the particles clear of the machine.
- The machine is delivered with a water cooling system for the cutting area.
- The machine is delivered with a conveyor including an automatic speed control depending on the rotating speed of the main motor.
- The machine is not direct driven so it is almost impossible to jam under normal use. In the event of solid matter being fed into the machine some protection of the rotating parts will result from the natural slip of the V-belt drive.

A cutter as discussed above with a capacity of 1000 kg PU/h has to be specially designed and built. According to information of the representative it is possible to up-scale a standard cutter to the appropriate size. Technical information about the upscaled Gran 2:

- Capacity: 1000 kg/h by reduction of 5 to 1 cm.
- Main motor: 150 kW
- Electrical supply required: 30 amp. isolator. 3 phase. 380/440 volts. 50 hz. or to customers specifications.

Price: The price of the cutter including speed control, conveyor and water cooling is Hfl. 250,000,--.

For more information on manufacturer and representative is referred to Appendix A5.XXIII

5.4.3 Cutter 3 & Mixing Vessel

After reducing the particle size the PU pieces are dumped into a vessel filled with MEG as solvent. The MEG is not only a solvent but also the reactant. Therefore the PU particles and MEG have to be mixed thoroughly. The mixer which is installed in the vessel is not an ordinary mixer; it is called a High Shear mixer or High Speed mixer. This mixer rotates with a very high speed and is therefore able to make a good dispersion of the MEG and PU. This high speed mixer induces high shear forces on the PU particles which tear the PU particles apart. Every time a PU particle passes the mixer its size will be reduced. During the reducing of the PU pieces gas escapes and leaves the dispersion. After mixing the MEG and PU for 45
Figure 5.4A: Weighing Units (Dosco).

Figure 5.4B: In-Line High Shear Mixer (Silverson)

Figure 5.5: Disintegration head with grooves (Silverson)
minutes all PU particles have a size of about 500 μm. The formed dispersion can now be pumped to a storage tank.

To be able to add the correct amount of MEG the PU in the mixing vessel has to be weighed. This is done by placing weighing units under the mixing vessel (See Figure 5.4A). Once the vessel is empty, the units are reset, the vessel is filled with a fixed amount of MEG. The PU is being added by the screw conveyor until a set-point is reached. The conveyor stops.

The mixing vessel contains 10 m³ dispersion which is too much for a normal high shear mixer. Therefore an in line high shear mixer is recommended. Figure 5.4B shows a picture of an in line mixer. The idea is to pump the dispersion around and around until the PU particles have a size of 500 μm. The other mixer in the vessel prevents sagging of the PU. The high shear mixer has to be fed continuously because otherwise the amount of PU in MEG will be too high and all the MEG will be sucked by the PU. Also blockage of the high shear mixer may occur. After 45 minutes the dispersion will be ready. This figure is based on tests performed by ICI and on information from mixer manufacturer. Then the high shear mixer will be used to pump the dispersion to the storage. Technical information on the recommended in line high shear mixer follows below.

Head: Disintegration head with grooves (see Figure 5.5)
Power: 30 kW
Speed of rotor: 3000 min⁻¹
Pipe diameter: 0.1 m
Price: 45,000 Dutch guilders

Cost of the complete mixing/cutting vessel is Hfl. 101,000.--
For cost calculations is referred to Appendix A5.XVII

For more information manufacturers is referred to Appendix A5.XXIII.
1 = Dosiergerät
2 = Wirbelschneckenkühler mit Flüssigstickstoffeinspeisung (LN₂)
3 = Feinprallmühle UPZ
4 = Autom. Alpine Filter
5 = Temperaturfühler

Farberklärung:
Türkis = Isolierte Anlagenteile.

Figure 5.6A: Cryogenic Cutting Unit (Van Vloten, Alpine)

Figure 5.6B: Coriolis Principle Dosing Unit
5.5 The Drying Options

Appendix A5.1 shows an overview of the 9 drying options and can be used as a guide for the next paragraphs. The scheme has to be read from left to right and every horizontal line is an option. The following paragraphs are named after the drying method and will discuss the options.

After the dispersion is made it is pumped to a storage tank. From there it will be transported to the reactor. At delivery of the big PU foam blocks a 1% mass percentage of water is assumed. The water has to be removed from the PU before the reactor is reached. Water causes byproducts like DADPM and UREA during the reaction. The PU foam can be dried in many different ways and in different places in the process. In this chapter an enumeration of 9 drying principles will be presented.

5.5.1 Cryogenic Drying & Cutting

Some compounds cannot be cut under normal conditions because they are weak, sticky, elastic or sensitive to heat. PU foam is one of those compounds. Its porous and elastic structure make it almost impossible to pulverise the foam under normal conditions. Minimum particle size obtainable with cutters as used earlier in the process (See 5.4.1 & 5.4.2) is about 10.0 mm. Even with high-speed rotating cutters it is not possible to completely pulverise the PU foam. Heat generated by friction in these cutters will lead to decomposition of the foam.

Optimum particle size reduction is obtained with non-elastic, solid compounds. Granulators as used in Figure 5.6A can reach particle sizes < 300 μm. Therefore stiffening of the PU foam structure by freezing it with liquid nitrogen (LN₂) makes cutting and/or pulverising possible again. Small scale laboratory tests carried out by the industry have proven that PU foam can be pulverised when it’s frozen. The yield is PU with a particle size < 500 μm. Tests carried out at the laboratory of the Department of Process Engineering of The Delft University of Technology have yielded comparable results.

The PU glasspoint is about -40°C. Since the boiling point of LN₂ is -196°C (under atmospheric circumstances) theoretically it should be possible to increase the amount of PU to be frozen with 1 kg of LN₂. However due to friction in the cutter the LN₂ consumption remains relatively high, about 1.5 kg LN₂/kg PU.

After the PU particle size has been reduced to a 10 mm diameter in the first two cutters it is fed to a conveyor. In this conveyor the PU is sprinkled with LN₂ and frozen. In the cutter the PU is pulverised and reheated to ambient temperature so both N₂ and H₂O evaporate and are removed. To avoid moisture being absorbed by the dry PU foam the whole process should be performed under N₂ atmosphere.

After the cutter a dry non-porous PU powder remains. This powder has to be mixed in a vessel with MEG to obtain PU:MEG = 1:10. Measurement of the PU mass flow
1 Nauta mixer
2 Automatically operated vacuum filter with purge gas reservoir
3 Cooling medium
4 Heat exchanger/condensor
5 Condensate
6 Vacuum pump unit
7 Gas inlet for atmospheric conditions

Figure 5.7: Nauta Mixer (Hosokawa Micron)
can be done continuously in a flow meter based on the Coriolis principle (See Figure 5.6B). The principle of operation is as follows: Within the mass flow meter, the bulk solids hit a measuring wheel, are flung outward by guide vanes, and leave the meter through a central outlet. As a result of the Coriolis forces, the acceleration of the bulk solids by the measuring wheel generates a reaction moment to be measured. A 1% measuring accuracy can be obtained. The mixing vessel also functions as a buffer so pumping of the suspension through the pre-reactor heat exchanger to the reactor can be done continuously.

The price of an installation that can handle 1000 kg/h PU is about Hfl. 350,000,--. Although LN$_2$ only costs about Hfl. 0.30 /kg due to high consumption this will make the process very expensive.

For more information on manufacturers is referred to Appendix A5.XXIII.

**Conclusion**

The main advantage of this option is that the whole process, cutting, pulverising and mixing can be performed continuously. Another advantage over the options to be dealt with later is the fact that laboratory tests have proven it to be working.

Disadvantage is the high LN$_2$ consumption which makes the process very expensive.

**5.5.2 Drying in a Nauta Mixer**

After cutting the PU blocks the PU pieces are blown by cutter 2 into a storage tank. A screw conveyor transports the PU pieces to a Nauta mixer. In the Nauta mixer the drying of the PU takes place.

A Nauta mixer is a conically shaped vessel with two screws in it (see Figure 5.7). The Nauta mixer is filled at the top and emptied at the bottom. The screws scrape the walls when the vessel is emptied so all the material is forced out. In a Nauta mixer material can be dried in two ways:

1. The vessel is equipped with double walls and between these walls steam runs to heat up the vessel and it’s contents (not shown in Figure 5.7). The screws achieve a homogeneous heat distribution in the material. The vessel is put under vacuum to achieve a lower evaporation temperature of water and to remove gasses. The water evaporates out of the PU and the dry PU can transported out of the vessel.

2. In the filled vessel a N$_2$ gas stream is injected at the bottom which dries the PU by desorption. This is the packed bed principle which will be discussed in section 5.5.7. This method is not often used because of construction problems.
Figure 5.8: Flow Sheet Bubble Dryer

Figure 5.9: Bubble Dryer Flowsheet
After drying the dry PU must not get in contact with air because water will be desorbed from the air and the PU will get wet again. Therefore the whole process after the Nauta mixer must be under \( N_2 \) atmosphere.

Drying in a Nauta mixer is a batchwise procedure. The high shear mixer has to be fed continuously because otherwise the amount of PU in MEG will be too high and all the MEG will be sucked up by the PU. After the Nauta mixer a storage is installed to convert the batchwise output into a continues one.

The high shear mixer reduces the PU pieces in 45 minutes (see 5.4.3). Therefore it is necessary that the loading of the mixer with PU must be completed after 40 minutes. This to be on the safe side. A screw conveyor is used for the transport of the PU from the storage to the high shear mixer.

After the reduction of the PU particle size the dispersion is pumped to another storage tank which converts the batchwise output of the high shear mixer into a continues flow to the reactor.

**Conclusion.**

This option has the following disadvantages:

1. Heating up the PU particles is very difficult because PU is an isolator.
2. The percentage of water in the PU (1 \%) is too low for vacuum drying (See chapter 5.5.4).
3. Hosokawa Micron, the producer of Nauta mixers, can not produce a vessel of 25 m\(^3\) which is the volume needed for 1000 kg PU.
4. Hosokawa Micron assures that drying with \( N_2 \) will cause construction problems in the Nauta mixer.

On account of these disadvantages and the doubts of Hosokawa Micron, for using a Nauta mixer for the drying of the PU, this option is rejected.

For more information on manufacturers is referred to Appendix A5.XXXIII.

**5.5.3 Bubble Dryer**

In this option water is removed by stripping the dispersion with a gas flow. The corresponding flowsheets for this option are given in Figures 5.8 and 5.9. According to both flowsheets the crude PU is cut in the two main cutters. In Figure 5.8 a storage is installed between the mixing vessel and the cutters to assure continuous cutting and supply of the PU to the batch wise operated mixing vessel. In Figure 5.9 an extra mixing vessel is installed.

In both options the PU particles are mixed with MEG in the mixing vessel as described in 5.4.3. After all the PU is added to the mixing vessel, a gas flow is blown through the dispersion to remove the water from the MEG. Due to the hygroscopic behaviour of MEG it is assumed that the water has moved from the PU
Figure 5.9a Graphical representation of the strip process.
into the MEG. At the top of the mixing vessel the gas stream is removed and dried in a gas dryer. Because the vapour pressure of water (in MEG) is higher than the vapour pressure of pure MEG, the water concentration on the gas-liquid interface will be higher than the MEG concentration at the same interface. The vaporized water is removed with the gas stream. Since the difference between the vapour pressures is small a little MEG also will vaporize. The amount of MEG that vaporizes will be neglected in the next calculations.

To get a good water removal the temperature of the MEG has to be as high as possible because the vapour pressure of water increases at higher temperature. At a temperature of 160°C starts the reaction so the upper limit temperature is 150°C (10°C safety margin). When the required amount of water is removed, the content of the mixing vessel is transported to the pre-reactor storage. The dispersion will be heated to 200°C before entering the reactor.

5.5.3.1 Theory of the Stripping Process

The basics of this stripping process is mass transfer in a gas-liquid system over an interface. In figure 5.9a is given a graphical representation of this mass transfer process. The mass transfer process will be calculated with different models. To model mass transfer and stripping processes some assumptions have to be made. These assumptions are:

A  The concentration of water in the liquid is always in equilibrium with partial pressure of water in the bulk of the gas. This means that there is no pressure drop in the gas phase and infinitely fast equilibrium. This absorption equilibrium can be described with Henry’s law:

\[ y \cdot P = x \cdot He \]  \hspace{1cm} (5.4)

In equation (1) the concentrations of water are expressed in mole fractions \( x, y \) (mol water/mol gas and mol water/mol liquid). Practically it is better to express the concentrations in kg/m³ or mole/m³ and convert \( He \) to \( m \) (volumetric distribution coefficient).

\[ m = \frac{[H_2O]_{gas phase}}{[H_2O]_{liquid phase}} \]  \hspace{1cm} (5.5)
Figure 5.10: Henry Coefficients
According to Wesselingh [1] this conversion is:

\[ m = \frac{H_e}{P} \frac{M_{\text{MEG}}}{M_{N_2}} \frac{\rho_{N_2}}{\rho_{\text{MEG}}} \]  

(5,6)

The concentration at the interface is given by:

\[ c^* = m * c_i \]  

(5,7)

B. At a certain distance from the surface the concentration of water in the liquid becomes independent of distance and equals to \( c_i \). This means that there is only a concentration profile in the gas-liquid film and one concentration of water in the liquid phase and one in the gas phase. Both gas and liquid phase are considered perfectly mixed as given in the model above.

C. In all models is assumed that the mass transfer resistance is in the liquid phase. This also supports the assumption mentioned at 2. There is only mass transfer over the interface.

D. The temperature of the liquid is the same as the temperature of the gas and the pressure is 1 bar.

E. The Henry coefficient (\( H_e \)) of water in MEG is unknown, but the Henry coefficient of water in DEG (diethylene glycol) is well known. Because of the similarity between MEG and DEG the assumption is made that the Henry coefficients do not differ very much. The Henry coefficient of water in DEG as a function of temperature is given in Wesselingh[1] This is given in Figure 5.10.

F. The diffusion coefficient of water in MEG as a function of temperature is unknown. The diffusion coefficient is calculated by using the Tyn and Calus method and the Nakanishi correlation. These correlations are given in Reid[2]. In Appendix A5.II the diffusion coefficient is calculated using the two methods at a temperature of 140 °C. The difference between the estimated diffusion coefficients is very small. For the calculations the diffusion coefficient calculated with the Nakanishi correlation is used. According to Reid [2] the Nakanishi correlation gives the best estimation for polar solvents.

G. The volume fraction of gas in the gas-liquid system is arbitrarily chosen \( \varepsilon = 0.3 \). According to Wesselingh[1] and Bleek[3] for a well mixed vessel;

\[ 0.2 < \varepsilon < 0.4. \]
H. During stripping $V_{\text{liquid}}$ and $V_{\text{gas}}$ remains constant. This means that there is minimum evaporation and the volume of the gas does not change by the transferred water.

I. The total surface area $S_{\text{tot}}$ is given by:

$$\frac{S_{\text{tot}}}{V_{\text{gas}}} = \frac{6}{d_b}$$

(5.8)

Assumed is that $d_b = 2 \times 10^{-3} \text{ m}$.

5.5.3.2 Description of the Different Models

To calculate the mass transfer process three models are used:

1. Film model (Lewis and Whitman model)
2. Penetration model (Higbie model)
3. Surface renewal model (Danckwerts model)

A detailed survey of these models is given in Bleek[3].

5.5.3.2.1 Film model.

In this model a stagnant liquid film exists at the interface in which only H$_2$O moves as a result of molecular diffusion. This diffusion is described by Fick's law. The thickness of the film $\Delta$ is chosen in such a way that no transport-resistance is experienced outside this film. From Fick's law follows:

$$\phi = D_{\text{wm}} \ast S \ast \left(\frac{dc}{dx}\right)_{x=0}$$

(5.9)

The way in which $c$ changes with distance $x$ can be found by solving the mass-balance for a slice with thickness $dx$, parallel to the interface, and integration between the boundaries;

$x = 0$, $c = c^*$ and $x = \Delta$, $c = c_g$

The mass balance and the integration are given in Bleek[3]. Only the result is given here.

$$c = c^* - (c^* - c_g) \ast \frac{x}{\Delta}$$

(5.10)

Together with equation (6) the flux $\phi$ for the film model becomes:
The flux calculated with this model is used in the stripping process as the amount of transported water from one phase to the other phase. According to Newton’s law the flux can also be written in the form:

\[ \phi = K_{fl} S_{tot} (c^* - c_g) \]  

(5.12)

The stripping process can be described with a mass balance of water in the gas phase and a mass balance for the MEG phase. Simultaneous solving of these balances gives the desired concentrations. These mass balances are describing the changes of the water concentration in the phases.

Gas phase:

\[ V_{gas} \frac{dc}{dt} = \phi_v (c_0 - c_g) + K_{fl} S_{tot} (m \cdot c_t - c_g) \]  

(5.13)

Liquid phase:

\[ V_{liq} \frac{dc_i}{dt} = -K_{fl} S_{tot} (m \cdot c_t - c_g) \]  

(5.14)

These two differential equations are solved with the programm PSIE. According to Bleek[3] it is impossible to obtain the value of \( \Delta \) from the model. In practice it is calculated from experimental mass transfer measurements. According to Bleek[3] \( \Delta = 10^{-4} \text{ m} \) is a good estimation. The corresponding programm setup is given in Appendix A5.III

5.5.3.2.2 Penetration model.

In this model it is assumed that the interface is refreshed continuously by fresh packets of liquid from the bulk. Each of these packets remain at the gas-liquid interface for the same time \( \Theta \) and then disappear in to the bulk. During its stay at the interface the transport of water is described by non-stationary diffusion into a semi-infinite medium. A visualisation of this model is given in Appendix A5.IV. According to Bleek[3] the constant-time \( \Theta \) can be calculated with:

\[ \theta = \frac{db}{u_g} \]  

(5.15)

The contact between gas and liquid is described as a "plug-flow" contact.
Figure 5.11: The water concentration in the MEG-phase as a function of time for three different models when the $\phi v = 3000 \text{ m}^3/\text{h}$.

Figure 5.12: The water concentration in MEG for $\phi v = 1000 \text{ m}^3/\text{h}$. 
From the definition of non-stationary diffusion and the mass balance over a slice in the packet of liquid at the interface a derivation for the mass flux is possible. This derivation is rather complex and is given in Bleek[3] and Smith[4]. Only the result is given in equation (13);

\[ \phi = 2 \sqrt{\frac{D_{wm}}{\pi \cdot \theta}} \cdot S_{tot} \cdot (c^* - c_g) \]  

(5.16)

Writing in the form according to Newton's law;

\[ \phi = K_{L_{high}} \cdot S_{tot} \cdot (c^* - c_g) \]  

(5.17)

For the stripping process the same equations (10) and (11) are valid when instead of \( K_{L_{film}} \) \( K_{L_{high}} \) is used. The stripping process with the new \( K_{L} \) value is also calculated with the program PSIE. The program setup for this model is given in Appendix A5.III.

**5.5.3.2.3 Surface renewal model (Danckwerts model).**

This model is an alternative reading of the penetration-model. The packets of liquid are no longer considered to be at the interface for one specified time \( \theta \), but all values between 0 and \( \infty \) seconds are possible. This means there is a distribution of contact-time at the interface. The chance that a packet of liquid leaves the interface is equal for all packets and independent of the time it stays at the interface. The contact between gas and liquid can be described as an "ideal-tank" contact. Also the resulting flux is given here. The derivation is given in Bleek[3]. the corresponding flux for this model is:

\[ \phi = \sqrt{D_{wm} \cdot S_{new}} \cdot S_{tot} \cdot (c^* - c_g) \]  

(5.18)

In Newton law's form:

\[ \phi = K_{L_{Danck}} \cdot S_{tot} \cdot (c^* - c_g) \]  

(5.19)

Identically the stripping process is calculated with this model on the same program PSIE. The programm set up is given is Appendix A5.III.

**5.5.3.3 Results of These Stripping Process Calculations**

With this strip process it is tried to reduce the water fraction in the MEG phase with at least 50 % to meet de required specifications. This reduction has to be made in a short period of time. With this calculation the gasflow is changed to meet the required water fraction in a certain period of time. For a drying time of 15-20 minutes the gasflow has to be 3000 m\(^3\)/h. In Figure 5.11 the changing of the water
Figure 5.13: The water concentration as a function of time in the ICI-vessel
setup is given in Appendix A5.III. This is a highly unrealistic gasflow. This kind of gas flow requires special equipment for handling and maintenance (pumps, gasdryer, gas distributer, pressure drop ed).

With a lower gasflow, say $\phi = 1000 \text{ m}^3/\text{h}$ the drying time is about 1 hour.
In Figure 5.12 and Appendix A5.V the corresponding water concentration in MEG is given. The specifications are met first for the Higbie model at a time of 3300 s. According to the other models the drying time is much longer. This means that 1000 kg PU in dispersion is dried in 1 hour. For a throughput of 1000 kg/h three parallel mixing vessels are needed each with an operation cycle of 3 hours.

The used models and parameters are checked with experimental measurements by ICI. In the ICI experiment 35 kg PU was dispersed in 35 kg DEO and heated to 200 °C. Through the dispersion flows a $N_2$ gasflow of 1 m$^3$/h. In 15 minutes the water concentration is halved. With the described model this experiment is simulated with PSIE, when the calculated drying time approaches the measured drying time (15 minutes = 900 seconds) the used models are correct.

For this calculation the same assumptions as described in 5.5.3.1 are made. The diffusion coefficient of water in DEO at 200 °C is again calculated the same way as mentioned earlier (Reid[2]). This calculation is given in Appendix A5.VI. The used program set up is given in Appendix A5.VII. In Figure 5.13 the water concentration in MEG is given for the three models for the ICI experiment. From Figure 5.13 can be seen that the three models do not differ very much and the drying time is about 900 s (15 minutes) as measured in the experiments. Therefore the used models and parameters are correct.

Conclusion.

The results of this calculation shows that it is possible to halve the water fraction and meet the specification in the required time of 900 s. To reach this water fraction the gasflow has to be 3000 m$^3$/h or 3 mixing vessels are needed.

The advantages and disadvantages of drying in a bubble dryer are given below.

Advantages:

1. No new equipment are needed, drying occurs in the mixing vessel by a gas distributor. Mixer and dryer are combined in a single vessel.
2. The MEG has to be preheated before entering the mixing vessel. The used heat exchanger is smaller than the heat exchanger needed to heat the dispersion, because it is easier to heat up the liquid than to heat up a dispersion.

Disadvantages:

1. The required amount of gas is very high 3000 m$^3$/h (or 1000 m$^3$/h) and the water concentration in the gas is very low. This means that the used gasdryer is very expensive when the water has to be removed from the gas.
The reached water concentration is 0.5 kg/m$^3$. To reach a lower water concentration the gasflow has to increase a lot.

The mixing vessel and the pre reactor storage have to be isolated very well to keep the heat loss as low as possible.

At a temperature of 140°C and a gasflow of 3000 m$^3$/h (or 1000 m$^3$/h) there will also evaporate much MEG. The effect of MEG on the gas dryer is unknown and there is an explosion hazard when MEG and air at a temperature of 140°C are mixed by mistake.

This process requires many operational procedures after each other, therefore the controlling becomes very complex.

On account of these disadvantages the bubble drying option is rejected.

5.5.4 Vacuum Dryer

In this option the PU is dried in a vessel under high vacuum. After cutting of the PU foam blocks in the two cutters the PU is transported to the vacuum drying vessel. The vacuum vessel operates batchwise. Therefore a PU storage needed to assure continuous cutting in the cutters. After drying in the vacuum dryer the PU is transported with a screw-conveyor to the mixing vessel with the inline high sheer mixer. This transport has to be under N$_2$ atmosphere and any contact with the surrounding air has to be avoided, because the moisture in the air will be absorbed by the dry PU. After the dispersion is made in the mixing vessel it is transported with a pump to the pre reactor storage to assure a continuous stream to the reactor. Before entering the reactor the dispersion is preheated in the heat exchangers to a temperature of 200°C.

5.5.4.1 Vacuum Dryer

In vacuum dryers the boiling-point of water is lowered below 100°C by reducing the pressure. Normally if the atmospheric pressure is reduced 100 times, the boiling point will be around 0°C according to Sokhansanj[7]. The degree of vacuum and temperature for drying depend on the sensitivity of the material to drying rate and temperatures. Because of the reduced pressure, transfer of heat depends on methods other than convection. In practice radiation and/or conduction are used. According to Woods[10]. Flexible PU-foam is an isolator and has a very poor heat conductivity. Therefore heat transfer to the PU foam is very difficult. Besides that, PU foam is also heat sensitive. From experiments carried out with the PU foam in the laboratory it is has shown that PU degrades after a while when it is exposed to a high temperature (≥ 70°C) in an oven. Therefore the PU has to be dried under vacuum at low temperature. Temperatures ranging from 35 to 60°C are normally used.

5.5.4.2 Pressure for Vacuum Drying

It is assumed that the water in the PU is not in liquid-phase but absorbed by the PU molecules. This means that the pressure needed for drying is lower than the vapour pressure of pure liquid water at that temperature. The pressure can be calculated with the modified Raoults law.
<table>
<thead>
<tr>
<th>$T$ [°C]</th>
<th>$P_{\text{vap}}(T)$ [Bar]</th>
<th>$P$ from (5.20) [$10^{-3}$ Bar]</th>
<th>$P$ from (5.22) [$10^{-3}$ Bar]</th>
</tr>
</thead>
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<tr>
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<td>3.116</td>
<td>3.424</td>
</tr>
</tbody>
</table>

Table 5.2
Po/y Urethane Recycling

Feed

\[ y m_{H_2O} P = x m_{H_2O} \gamma_{H_2O}^* P^{vap}(T) \]  

(5,20)

Where \(x_m, y_m\) are mass fractions of water. Assuming the system is ideal and no PU is present in the vapour so

\[ y m_{H_2O} = 1 \quad \text{and} \quad \gamma_{H_2O} = 1 \]

With this equation (5,20) simplifies to:

\[ P = x m_{H_2O} P^{vap}(T) \]  

(5,23)

The use of the mass fraction in stead of the mole fraction is much better because the mole fraction is only valid when the sizes of molecules are in the same range. PU molecules are much larger than the water molecules therefore the water molecule interacts with a small part of the PU molecule. Sometimes it is even advisable to use volume fraction of water in the PU. The corresponding Raoult equation becomes:

\[ P = x v_{H_2O} P^{sat}(T) \]  

(5,24)

The volume fraction can be calculated with:

\[ x v_{H_2O} = \frac{x m_{H_2O}}{x m_{H_2O} + (1 - x m_{H_2O}) \frac{\rho_{H_2O}}{\rho_{PU}}} \]  

(5,25)

In Table 5.2 the corresponding drying pressures are calculated with equation (5,20) and equation (5,24) for different temperatures. Assumed that the mass fraction of water is: \(x m_{H_2O} = 0.01\) and that the densities of water and PU remain constant in this short temperature range.

For \(\rho_{H_2O} = 1000 \text{ kg/m}^3\), \(\rho_{PU} = 1100 \text{ kg/m}^3\) the volume fraction becomes \(x v_{H_2O} = 0.01099\)

Conclusion.

The advantage and disadvantages of the vacuum drying option are given below.

Advantage:

1. It is possible to dry at a low temperature where few heat input is needed.
Figure 5.14: Flash Dryer Flowsheet
Disadvantages:

2. The required pressures for vacuum drying are given in Table 5.2 are in the range of 0.2 - 3 mbar (0.1 - 2.2 Torr). According to Gutherie[11] this pressure is in the range of medium vacuum, for which installation are extremely expensive.

3. According to Sokhansanj[7] is vacuum drying one of the most expensive methods of drying.

4. The drying time is unknown and only experimentally determinable. According to Sokhansanj[7] and Gardner[12] drying time depends on the properties of the dried material.

5. Vacuum vessels are small vessels. According to Moore and Table A5.VIII.1 given in Appendix A5.VIII the maximum capacity of a rotary vacuum dryer (the most used and satisfactory vacuum dryer) is 15 m³. For a drying time of 1 hour and a throughput of 1000 kg/h (50 m³/h) PU there are at least 4 vacuum dryers needed.

On account of this disadvantages the vacuum drying option is rejected.

5.5.5 Drying in a Flash Vessel

In this option water is removed by flashing the dispersion in a flash vessel. The process flowsheet is given in Figure 5.14. The dispersion is made the same way as described in 5.4.3. The PU contains 1% of water. In the dispersion is 10 kg (0.55 kmol) assuming all the water is transferred from the PU to the MEG. The dispersion is stored in the pre-reactor storage. Before the dispersion enters the flash vessel it is heated in a heat exchanger. The pressure in the flash vessel is lower and therefore a new gas-liquid equilibrium is reached. As a consequence the gas-liquid separation takes place.

Because the volatility of water is higher than the volatility MEG most of the water will evaporate. The solubility of water in MEG is very good and according to Katz[13] the vapour pressure of water in MEG (and DEG) is much lower than the vapour pressure of pure water. An amount of MEG will also evaporate. This highly non-ideal system is simulated with the program ChemCad to calculate the reached gas-liquid equilibrium. In the ChemCad calculation the effect of solid PU particles on MEG-water behaviour is totally neglected and the flash is considered a binary system.

The specification for the feed of the reactor is that the water fraction is less than 0.05%. The water fraction in the dispersion before the flash is \( \approx 0.1 \% \). There are two factors limiting this flash:

1. The temperature of the dispersion has to be kept below 160 °C. At a temperature of 160 °C the reaction between MEG and PU starts.
Therefore the temperature of the dispersion will always be below 150 °C (10 °C safety margin).

2. The amount of evaporated MEG has to be as low as possible. When the amount of MEG in the dispersion becomes too low there are problems with the transport of the dispersion to the reactor.

5.5.5.1 Flash Calculation

The flash calculation is based on the fact that a liquid under pressure passes through a valve to a pressure low enough so that some of the liquid vaporizes or "flashes", producing a two-phase stream of vapour and liquid in equilibrium. In this case we consider two types of flash calculations.

5.5.5.1.1 Adiabatic flash at fixed pressure.

With an adiabatic flash no heat is transferred to the surrounding and the energy needed to vaporize some of the liquid is supplied by the enthalpy of the feed (the temperature of the liquid drops). The flash calculation is made at a fixed pressure and the temperature changes as a result of evaporation.

In the flash there is no conversion and loss of material. Therefore the material-balance equations is:

\[ F = G + V \]  \hspace{1cm} (5,26)

\[ F \cdot z_i = G \cdot y_i + L \cdot x_i \]  \hspace{1cm} (i=1,2) \hspace{1cm} (5,27)

The vapour-liquid equilibrium is generally described by the Rault's law

\[ y_i = K_i \cdot x_i \]  \hspace{1cm} (i=1,2) \hspace{1cm} (5,28)

where \( K_i \) is the K-value

In this flash calculation the K-value model of Soave-Redlich-Kwong (SRK) is used. This model is available in the ChemCad library. See ChemCad[14] and Smith[15] for more information on this model.

With an adiabatic flash the enthalpy balance is

\[ \sum_i \Phi_i \cdot H_i(T_{in}) - \sum_i \Phi_i \cdot H_i(T_{out}) - \sum_i \Phi_i \cdot x_i \cdot H_i(T_{out}) = 0 \]  \hspace{1cm} (5,29)

The model to calculate the enthalpy is also the Enthalpy Model of Soave-Redlich-Kwong see ChemCad[14]. A simplification of this enthalpy balance is the given heat balance (5,30).

5.21
REMOVED WATERFRACTION AT DIFFERENT $T_f$

at a vessel pressure of 75 mm HG

![Graph showing removed water fraction at different $T_f$ values at a vessel pressure of 75 mm HG.](image)

Figure 5.15: Removed Waterfraction (Different $T$)

---

REMOVED WATERFRACTION AT DIFFERENT $P$

$T_{feed}$ is 150 °C

![Graph showing removed water fraction at different $P$ values with $T_{feed}$ at 150 °C.](image)

Figure 5.16: Removed Waterfraction (Different $P$)
released heat = heat for evaporation

\[ \sum_i \Phi_{F_i} \cdot C_P (T_{in} - T_{out}) = \sum_i \Phi_{V_i} \cdot H_{vap}(T_{out}) \]  

(5.30)

5.5.5.1.2 Isothermal flash at fixed pressure.

For an isothermal flash the heat needed to vaporize is supplied from an external heat source \( Q_{ex} \). The enthalpy balance is:

\[ Q_{ex} = \sum_i \Phi_{V_i} \cdot H_i(T_{out}) - \sum_i \Phi_{L_i} \cdot H_i(T_{out}) + \sum_i \Phi_{F_i} \cdot H_i(T_{in}) \]  

(5.31)

An isothermal flash is not a real flash operation but the gas-liquid equilibrium in an evaporator at a fixed pressure. The material balances equations and K-value calculation are the same for the isothermal flash as for the adiabatic flash and given by equations (5.26), (5.27), (5.28). Iterative solving of these equations gives the desired results, the gas phase( \( y_i \)) and the liquid phase (\( x_i \)).

\[ \sum_i x_i = \sum_i y_i = 1 \]  

(5.32)

5.5.5.2 ChemCad Flash Calculation

The vapour-liquid equilibriums of this flash are found by simulation of the program ChemCad. In ChemCad the equipment PLAS is chosen to simulate. There are three streams connected to this PLAS. The flowsheet summary and flash summary are given in Appendix A5.IX.

With CHEMCAD two kinds of flash calculation are simulated:

1. Adiabatic flash with a fixed pressure in the vessel
2. Isothermal flash with a fixed pressure and temperature in the vessel

5.5.5.2.1 Optimum feed temperature \( T_{feed} \)

The best process conditions of these flashes are found by changing the pressure in the vessel and temperature of the feed at an adiabatic flash and comparing the result with an isothermal flash. At the best process condition at least 50 % of the water in the feed is removed together with a minimum amount of MEG.

In Figure 5.15 the removed water fraction is given as a function of the feed temperature for a fixed vessel pressure \( P_{vessel} = 75 \text{ mmHg (0.1 bar)} \). Figure 5.15 shows that a higher temperature improves the separation. At \( T_{feed} = 145^\circ \text{C} \) the specification of 50 % removal just is reached. The upper limit of the temperature is 150 °C, as mentioned before. At other pressures the same results are found. In Appendix A5.X the results are given for 4 different vessel pressures (P=75 mmHg, P=50 mmHg, P=76
MASS RATIO H2O : MEG IN TOP

Figure 5.17: Mass Ratio H2O, MEG in Top

Combination mass fraction & mass ratio

Figure 5.18: Combination Mass Fraction & Mass Ratio
mmHg, P=74 mmHg). For a good separation it is the best to keep the feed temperature at 150 °C.

5.5.5.2.2 Optimum vessel pressure $P_{\text{vessel}}$

To get a better picture of this separation the pressure in the flash vessel is changed to a fixed feed temperature $T_{\text{feed}}=150$ °C. In Figure 5.16 the removed water fraction is given as a function of the vessel pressure. From Figure 5.16 can be noted that a lower pressure improves the separation of water. A low vessel pressure seems better for the operation of the separation vessel.

Not only does a lower pressure improve the separation process also more MEG will evaporate. In Figure 5.17 is shown the mass ratio water/MEG as a function of the vessel pressure. It shows that at a lower pressure relatively more MEG than water evaporates. This implies that a higher pressure is better. For safety and economic reasons it is best to operate under a higher pressure close to atmospheric pressure (a greater all thickness, greater vacuum pump, expensive pressure control system). Besides the recovery of MEG the flash becomes more difficult and more expensive when relatively more MEG evaporates because the water concentration in the MEG reduces.

This seemed to be a contradiction with results from Figure 5.17. The optimum pressure is a pressure which is somewhere between these two observations. In Figure 5.18 are both Figure 5.16 and Figure 5.17 put together and an optimum is found at $P_{\text{vessel}} = 75$ mmHg.

5.5.5.3 Flash Calculation Results

The results of the adiabatic flash with $P_{\text{vessel}} = 75$ mmHg and $T_{\text{feed}} = 150$ °C is given in Appendix A5.XI. The top and bottom streams are:

Top

Total = 6.3739 Kmol/h with 6.01 Kmol/h (372.6 kg/h) MEG
0.35 Kmol/h (6.55 kg/h) water

Bottom

Total = 155.29 Kmol/h with 155.1 Kmol/h (9616.2 kg/h) MEG
0.19 Kmol/h (3.45 kg/h) water

In this condition it is possible to remove 65.6 % of the water in the feed and satisfy the required specification (50 %).
The results of the isothermal flash with $P_{\text{vessel}} = 75$ mmHg and $T_{\text{vessel}} = 140$ °C are given in Appendix A5.XII. The top and bottom streams are:

**Top**
- Total = 15.67 Kmol/h with 15.33 Kmol/h (958.7 kg/h) MEG
- 0.346 Kmol/h (8.36 kg/h) water

**Bottom**
- Total = 145.99 Kmol/h with 145.9 Kmol/h (9049.4 kg/h) MEG
- 0.09 Kmol/h (1.64 kg/h) water

This isothermal flash makes it possible to remove 83.6% of the water in the feed. This also meets the demanded of 50% removal. The isothermal flash is not a realistic option because the evaporated amount of MEG is very high (about 10% of the feed) and the water concentration is very low. Therefore the recovery of the MEG is more difficult.

This option required an external heat source with a heat duty of 114.313 MJ/h. All these reasons makes the isothermal flash a more expensive option (both equipment and operation).

The best option is an adiabatic flash at $P = 75$ mmHg (0.1 bar) and the $T_{\text{feed}} = 150$ °C. As mentioned before this option meets the desired specifications.

**5.5.5.4 Design Flash Vessel**

The design of the flash vessel is made by the design procedure given in Olujic[16] and Coulson[17]. The calculation of the vertical flash vessel dimensions are given in Appendix A5.XIII. The results of this design are:

- $D_{\text{vessel}} = 0.495$ m (diameter)
- $H_{\text{vessel}} = 9.715$ m (height)

According to Olujic[16] is a proper design when

$$3 < \frac{D_{\text{vessel}}}{H_{\text{vessel}}} < 5$$  \hspace{1cm} (5,33)

For the flash vessel mentioned above is $H_{\text{vessel}}/D_{\text{vessel}} = 20$ and completely of the given range. This deviation is caused by the too high design gas velocity: $U_{\text{gas}} = 2.3$ m/s. To improve this design two possibilities exist:

1. Vertical flash vessel with $H_{\text{vessel}}/D_{\text{vessel}} = 3$ and a different gas velocity.
2. Use of an Horizontal flash vessel.
Fig 5.19: The dimensions of the vertical flash vessel

Fig 5.20: Dimensions of the horizontal flash vessel
5.5.5.4.1 Improved vertical flash vessel.

The design of this vessel has the same design equations as mentioned in Olujic[16] and Coulson[17] with one exception. To calculate the $D_{\text{vessel}}$, the design parameter $H_{\text{vessel}}/D_{\text{vessel}} = 3$ is used in stead of the equation for design gas velocity $U_{\text{gas}}$:

$$U_{\text{gas}} = 0.035 \times \frac{\rho_{l}}{\rho_{v}}$$ \hspace{1cm} (5.34)

The new dimensions are: $D_{\text{vessel}} = 1.14 \text{ m}$ $H_{\text{vessel}} = 3.4 \text{ m}$

and $U_{\text{gas}} = 0.44 \text{ m/s}$. In Figure 5.19 all the dimensions are given.

5.5.5.4.2 Horizontal flash vessel.

No standard design equations are available for the design of the horizontal flash vessel. To get an proper design according to Gerunda[18], Olujic[16] the design parameter $L_{\text{vessel}}/D_{\text{vessel}} = 5$. With this and some design equations used for liquid-liquid separations the dimensions of the horizontal flash vessel are calculated in Appendix A5.XIV. The calculated dimension are given in Figure 5.20:

$D_{\text{vessel}} = 0.817 \text{ m}$ $L_{\text{vessel}} = 4.09 \text{ m}$

Both vessels have a wall thickness of 15 mm to resist the external pressure. In Appendix A5.XV are for the two vessels the critical buckling pressure calculated using the Brownell and Young correlation given in Coulson[17].

Two flash vessel designs are available for this flash option. According to Olujic[16] the performance of an vertical vessel is better than an horizontal vessel. So the best design is the vertical improved flash vessel.

5.5.5.5 Recovery of MEG

After the flash the MEG stream is condensed and has to be dried. A possibility to dry this stream is stripping with $N_{2}$ gas. The $N_{2}$ stream is dried in a gasdryer (Delair B.V produces gasdryers and their address is given in the list of companies at the end of the feed section part). In principal there are 3 kinds of strippers; tray column, random packing column and structured packing column. To make a decision which column to choose the next calculations are necessary:

Input:

<table>
<thead>
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<th>Component</th>
<th>Flowrate (kmol/h)</th>
<th>Conversion (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEG</td>
<td>6.00990</td>
<td>1.67</td>
</tr>
<tr>
<td>$H_{2}O$</td>
<td>0.32483</td>
<td>0.09</td>
</tr>
</tbody>
</table>

$x_{\text{in}} = 0.051$
Figure 5.20a McCabe-Thiele diagram

Figure 5.20b
A recovery of 98% of the H\textsubscript{2}O out of the MEG stream is possible:

\[ x_{\text{out}} = 0.001 \]

Given conditions: \( T = 139.24 \, ^\circ\text{C} \), \( P = 1 \, \text{bar} \), \( \text{He} = 0.4 \, \text{MPa} \) (see Figure 5.10).

\[ K = \frac{\text{He}}{P} = 4 \quad (5.35) \]

A minimal use of N\textsubscript{2} demands a stripping factor \( S = \frac{K \cdot G}{L} = 1 \)

This yields \( G = 0.44 \, \text{mol/s} \)

With \( M_{\text{N2}} = 28 \, \text{kg/kmol} \) this gives a N\textsubscript{2} flow of 44.4 kg/h:

\[ \phi_{\text{g}} = 44.4 \, \text{kg/h} \, \text{N}_2 \]

In the McCabe-Thiele diagram given in figure 5.20a the number of theoretical trays can be found:

Calculation lead to \( \frac{0.050 - 0.049}{0.200 - 0.196} = 13 \) theoretical trays.

**Tray column.**

The column efficiency, \( E_{\infty} \), is defined as:

\[ E_{\infty} = \frac{\text{theoretical number of trays}}{\text{real number of trays}} \]

Figure 5.21 gives with \( \chi = 0.062 \times \frac{\rho_s}{\mu_s K M_s} = 0.062 \times \frac{1100}{1.06 \times 4 \times 62} = 0.26 \)

\[ E_{\infty} = 30 \% \]

This makes the real number of trays: \( \frac{13}{0.3} = 43 \)

The calculations for a tray column are given in Table 5.3.

The height of the column is: \( H = 43 \times 0.15 + \text{a little bit extra} \)

A normal value for the top, bottom and the pipe fittings is 2 meters.
Flow factor: \( F_{lg} = \frac{\mu_l}{\mu_g} \left( \frac{\rho_g}{\rho_l} \right) \)

\[
F_{lg} = \frac{\mu_l}{\mu_g} \left( \frac{\rho_g}{\rho_l} \right)
\]

\[
= \frac{6.0099 \times 62}{0.32483 \times 28} \left[ \frac{0.82}{1100} \right] = 1.12
\]

Tray spacing: \( T_s = 0.15 \)

Capacity constant: \( C_g = 0.014 \) (see Figure 5.20b)

Flooding velocity: \( u_{g,max} = C_g \sqrt{\frac{\rho_l - \rho_g}{\rho_g}} \)

\[
= 0.014 \sqrt{\frac{1100 - 0.82}{0.82}} = 0.51
\]

Diameter: \( d = 1.2616 \sqrt{\frac{\mu_g}{\rho_g \times u_{g,max}}} \)

\[
= 1.2616 \sqrt{\frac{44.4}{3600 \times 0.82 \times 0.51}} = 0.22
\]

Table 5.3

<table>
<thead>
<tr>
<th></th>
<th>MEG [gram]</th>
<th>PU [gram]</th>
<th>PU : MEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input</td>
<td>Dispersion 56.55</td>
<td>1 : 16.4</td>
<td></td>
</tr>
<tr>
<td>Output</td>
<td>37.51</td>
<td>19.04</td>
<td>1 : 4.9</td>
</tr>
</tbody>
</table>

Table 5.4
So a tray column will be 8.5 meter high with a diameter of 0.22 meter.

**Random and structured packing column.**

Other calculations given in Appendix A5.XVI show the dimensions of a random packing and a structured packing column. The dimensions of the tray column being smallest and this column also being cheapest (see Appendix A5.XVII) the tray column is recommended.

**Conclusion.**

The advantages and disadvantages of drying in a flash vessel are given below.

**Advantages:**

1. 70 % of the water can be removed.
2. No complex equipment is necessary

**Disadvantages:**

1. Lot of equipment necessary.

On account of these advantages this option remains as a possible option.

**5.5.6 Drying After Filtration**

After cutting the PU blocks, like described in paragraph 1.1 and 1.2 the PU pieces are blown by cutter 2 to a storage tank. A screw conveyor transports the PU pieces to the mixing vessel. In the mixing vessel the PU blocks are reduced in 45 minutes to pieces of 500 micrometer, like described before.

The water has left the PU and is desorbed by the MEG during the mixing session. This desorption takes place because MEG is hygroscopic. The idea is to filtrate the MEG from the PU and than strip the water out of the MEG. After the drying of the MEG it is remixed with the PU to retain to the ratio of PU : MEG 1 : 10.

To get some insight of the behaviour of the dispersion during filtration, experiments have been done. First a dispersion was made by ICI with the ratio PU : MEG is 1 : 16.4. This dispersion is filtrated with 200 micrometer filtration paper and vacuum is used to achieve filtration. It is difficult to get a homogeneous filtercake so filtration will be very difficult in a continues process. The results of this experiment are tabled printed in Table 5.4.

Stated on this experiment the conclusion can be made that by the usual ratio of 1 : 10 only 50 % of the MEG can be filtrated. This mains that also only 50 % water can be removed. A higher percentage removed water can only be achieved by using more MEG in the dispersion. However, the MEG must be dried also and more MEG means a bigger stripper. It is also not practical to use a higher PU : MEG ratio
Table 5.5

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because the reactor needs a 1 : 10 ratio. Therefore a higher ratio leads to a purge flow of MEG.

Conclusion.

The already mentioned disadvantages of this option are summarized below.

1. Only 50 % of the water can be removed.
2. Filtration is difficult and will be more difficult in a continues process.

On account of these disadvantages this option is rejected.

5.5.7 Moving and Packed Bed Dryer

Both moving and packed bed dryer are based on the same drying principle. As can be seen in Figure 5.22, the flowchart of the moving bed option, the PU particles are fed to a large tank in which a dry gas stream is injected at the bottom. The moisture absorbed by the dry gas stream. The "wet" gas is dried in a gas dryer, reheated to the necessary temperature and blown through the dryer again. After drying is completed the PU particles are transported to the mixing vessel with a screw conveyor.

5.5.7.1 Drying Practice Moving Bed Dryer

The dryer basically has two parts:
- The upper part of the vessel functions as a buffer. The buffer has to be able to contain about 15 minutes of output of the pre-cutters so intermittent operation of the pre-cutters is avoided. The conveyor stops during emptying of the mixing vessel. Emptying takes approximately 15 minutes. Drying vessel here also functions as a buffer.
- The lower part of the vessel is the actual drying part, although in the buffer also drying takes place since the gas-flow never stops. During operation of the conveyor the PU slowly moves downward through the dryer.

Dimensioning of the vessel depends on the residence time of a layer of PU needed to meet the specifications \((x_o = 0.01, x_e =0.001)\). As discussed earlier with the Nauta dryer the major problem that has to be dealt with is the emptying of the drying vessel. To avoid bridge formation in the vessel the width is taken 2.5 m. At the bottom scrapers have to be installed that empty the vessel and feed the screw conveyor. The whole installation has to be grounded to minimise static charging of the PU. A schematic flowchart of the subsequent process steps is printed in Table 5.5.

5.5.7.2 Drying Practice Packed Bed Dryer

The principal difference between moving and packed bed dryer is discontinuous drying process (Compare Table 5.5 with table 5.6). To avoid intermittent operation of cutters 1 and 2 a storage is installed between the cutters and dryer. A basic process flow of the subsequent phases in the drying and mixing process can be seen in Table 5.6. The dryer is filled from the storage with PU particles. The vessel is
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Table 5.6
closed and within 30 minutes the PU is dried. Because the mixing vessel has to be filled slowly to avoid blockage of the high shear mixer with large PU particles a screw conveyor is used to transport the dry PU foam to the mixing vessel. The dryer is emptied in 30 minutes. Mixing takes 45 minutes. This to guarantee that all the incoming PU has passed the high shear mixer several times. After mixing the mixing vessel is emptied into the pre reactor storage.

5.5.7.3 Drying Theory Moving Bed Dryer

Again no experimental data are available on the drying behaviour of PU foam in a gas flow. Therefore a theoretical model is made by using the mass balance over a control volume of PU.

The average density of the crude PU is assumed to be 50 kg/m$^3$. 1000 kg/h has to be recycled, so the volume throughput is 20 m$^3$/h. The bed porosity is about 0.6 so the volume throughput increases to 33.3 m$^3$/h.

As can be seen in Table 5.6 drying time of a layer of PU is supposed to be about 30 minutes. The scrapers at the bottom of the tank do not influence the drying behaviour since they are installed below the gas inlet. All calculations are based on dry N$_2$ gas. In the moving bed dryer it is advisable to use air, because an open connection with the atmosphere exists at the top of the vessel. Since air contains 80% N$_2$ and air and air can be dried the same way as N$_2$ the outcome of the calculations should not differ significantly when air is used instead of N$_2$. The packed bed dryer is a closed system during drying.

Modelling the dryer

The moving bed dryer can be seen as a tube reactor. This tube reactor is simulated by a series of ideally mixed non-stationary tanks. For each tank the concentration of the incoming gas equals the concentration in the tank. In this case a chain of ten tanks is taken as approximation of the moving bed dryer. The PU transport compared to the gasflow is very low, so the PU in the tank does not move. Over each tank two mass balances can be drawn up; One for the gas phase and one for the solid phase. The model used at the gas-solid interface is the Film model.

Mass balances:

\[
\text{Accumulation} = \text{In} - \text{Out} + \text{Transfer}
\]

Gas phase: \[
V_{gas} \frac{dc_g}{dt} = \phi_g c_0 - \phi_g c_g + k_g A_{spec} \left( \frac{xmP_{vap}}{RT} - c_g \right) V_{vessel}
\]  

(6,10)

PU phase: \[
V_p \frac{dxm}{dt} = -k_g A_{spec} \left( \frac{xmP_{vap}}{RT} - c_g \right) V_{vessel}
\]  

(6,11)
Figure 5.23: The influence of the gas temperature on the drying of PU-foam in the last tank of the series for the moving bed $V_{droger} = 32.129 \text{ m}^3$, $\phi = 250 \text{ m}^3/\text{h}$.
Poly Urethane Recycling

For the derivation of kg is referred to Appendix A5.XVIII.

The water concentration can be written as:

\[ c = \frac{\alpha m P_{vap}}{RT} \]

This relationship is derived in 5.5.4.2.

Both differential equations are solved simultaneously by use of the program xxxxx. Listing of the program can be seen in Appendix A5.XIX. For several temperatures the results can be seen in Figure 5.23. The results are based on the last reactor in the line. The drying gas in this tank has the highest moisture content, so drying of the PU will take more time (worst case situation). For a gas temperature of 60°C the specifications can be met with half an hour (1800 s). Gas temperature should not be too high to avoid decomposition of the PU foam.

5.5.7.4 Drying Theory Packed Bed Dryer

The packed bed drying theory is the same as of the moving bed theory. Here the packed bed is also simulated with ten tanks in line. The same mass balances as used above can be used:

Mass balances:

\[ \text{Accumulation} = \text{In} - \text{Out} + \text{Transfer} \]

\[ V_{gas} \frac{dc_g}{dt} = \phi vco - \phi ve_g + kg A_{spec} \left( \frac{\alpha m P_{vap}}{RT} - c_g \right) V_{vessel} \]

Gas phase \hspace{1cm} \text{(6,13)}

PU phase:

\[ V_{solid} \rho \frac{dxm}{dt} = -kg A_{spec} \left( \frac{\alpha m P_{vap}}{RT} - c_g \right) V_{vessel} \]

\hspace{1cm} \text{(6,14)}

Both differential equations are solved simultaneously by use of the pascal program TRKUSER.PAS. Listing of the program can be seen in Appendix A5.XX

As can be seen in Figure 5.24, the performance of the packed bed dryer is only slightly less than the performance of the moving bed dryer. In Figure 5.25 the influence of the gas temperature on the drying behaviour can be seen.

Conclusion

Both moving and packed bed dryer easily meet the specifications. Nevertheless both options have a few major disadvantages:

- No experimental data are available for both methods
- Due to static charging it will be hard to empty the dryers.

5.30
Figure 5.26: Conveyor Dryer

Figure 5.27 Flowsheet conveyor dryer
Construction of the dryers is rather complicated, specially around the gas inlets. PU decomposition may take place.

5.5.8 Conveyor Dryer

Due to the problems to be expected with emptying both moving and packed bed dryer the conveyor dryer is investigated. One type of conveyor dryer is given figure 2.26. As can be seen in Figure 5.27, the foam particles from cutter 2 are fed continuously to the dryer. This type of dryer has three key features:
- Gentle physical handling of the product. This will reduce the problem of static charging of the PU particles.
- Close control of process conditions. Variable bed movement and controllable gas flow make this possible.
- Continuous drying. In our case this is not an essential feature since the mixing process is batchwise. It is nevertheless less labour-intensive than a batchwise drying method.

The two main problems that have to be dealt with are:
- Removal of the dried PU foam from the belt. Due to static charging, which will always occur, it may be hard to remove the foam from the belt at the delivery end. This problem can be avoided by grounding all drying equipment and installing a scraper at the end of the belt.
- The whirling of the light PU particles in the dryer. To minimise this problem only air-down dryers can be applied. The downward gas-flow presses the PU against the belt. The sideways whirling of the foam can be avoided by installing partitions on the belt.

Principle of drying

Again no experimental data are available on the drying behaviour of PU foam in an conveyor dryer. To be able to estimate dryer performance the following formula is used:

\[
L_{\text{bed}} = \frac{-\phi_{\text{solid}}RT}{1.0 \times 10^{-3} M_{H_2O} k g A_{\text{spec}} H_{\text{bed}} W_{\text{bed}} (x m P_{\text{w}} - c_e R T)} dx
\]

This formula for the determination of bed length \(L_{\text{bed}}\), at a known bed height \(H_{\text{bed}}\), is based on the mass balance over a certain control volume of the dryer. For the derivation of this formula is referred to Appendix A5.XXI. This equation is solved for several situations on MathCad. See Appendix A5.XXI for a listing of the program. For the calculations \(N_2\) is used as drying agent. In Table 5.7 the bed length is printed for several different cases. The dryer has a width of 3.0 m.

As can be seen \(T_{\text{gas}}\) has to be high to minimise the length of the dryer. The problem with these temperatures is the possibility of degradation of the PU during drying. Another drawback of this dryer is the extremely high gas throughput. In case of a \(T_{\text{gas}} = 273\) K and \(u = 0.10\) m/s a gasflow of \(\phi = 2.0 \times 10^4\) m\(^3\)/h is necessary.
The influence of the gasflow on the drying of PU-foam in the last tank of the serie. Fixed bed met $V_{\text{dryer}} = 50 \text{ m}^3, T_{\text{gas}} = 60 \ ^{\circ}\text{C})$.

The influence of the gas temperature on the drying of PU-foam in the last tank of the serie fixed bed model met $V_{\text{droger}} = 50 \text{ m}^3, T_{\text{gas}} = 60 \ ^{\circ}\text{C})$. 
Therefore it is advisable to use dried air as drying gas.

Conclusion

The only advantage of this dryer is that the emptying problems like in the moving and packed bed dryer are avoided. This option has however a few major disadvantages:
- Gas temperatures need to be high or the dryer becomes excessively large.
- When N\textsubscript{2} is used as drying agent a large (and expensive) gas dryer and recirculation system has to be installed.
- The conveyor dryer is very expensive compared with the other options. A dryer with a floor area of 100 m\textsuperscript{2} costs roughly Hfl 2.500.000,-.
<table>
<thead>
<tr>
<th>Temperature (T)</th>
<th>V(_{\text{gas}} = 0.10 \text{ m/s} )</th>
<th>V(_{\text{gas}} = 0.20 \text{ m/s} )</th>
<th>V(_{\text{gas}} = 0.30 \text{ m/s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>293 K</td>
<td>6200 m</td>
<td>4150 m</td>
<td>3280 m</td>
</tr>
<tr>
<td>333 K</td>
<td>291 m</td>
<td>191 m</td>
<td>150 m</td>
</tr>
<tr>
<td>353 K</td>
<td>85 m</td>
<td>55 m</td>
<td>43 m</td>
</tr>
<tr>
<td>373 K</td>
<td>29 m</td>
<td>19 m</td>
<td>14 m</td>
</tr>
</tbody>
</table>

Table 5.7
5.6 Conclusion

In this chapter nine different drying options are mentioned. The advantages and disadvantages of all these options are also described. On the basis of these advantages and disadvantages 6 options are rejected and 3 remain options. These are

1. Cryogenic grinding
2. Drying in flash vessel
3. Drying in conveyor dryer

To make the best choice between these 3 options several selection criteria are compared: Performance, Price

5.6.1 Performance

5.6.1.1 Cryogenic Grinding Option

The fraction of water that remains in the PU after expansion and removal of the Nitrogen is unknown. During expansion water will evaporate but the amount of water removal is not measured by the manufacturer. This company has experimented with cryogenic grinding of PU foam.

The dispersion that can be made with this option has the appropriate structure. The PU particles all have a diameter < 500 μm.

5.6.1.2 Flash Option

The amount of water that remains in the dispersion is 30 % of the original amount of water. This amount of water is lower than the maximum water fraction (50 % of the original amount) allowed. When the pressure in the flash vessel is reduced 50 mmHg (0.07 Bar) the water removal will improve to 80 % (see Appendix A5.X). This process makes this option very flexible.

5.6.1.3 Conveyor Dryer Option

The design of the conveyor dryer is based on the fact that 10% of the original amount of water remains in the dry PU-foam. This meets the required specification of 50 % water removal. By changing the bed length, PU and/or gas flow and temperature of the gas the fraction of removed water can be changed. This drying method is also very flexible.

Based on the removed water fraction the flash option and the conveyor dryer option are the best choice, the conveyor dryer is even better.
<table>
<thead>
<tr>
<th>Drying option</th>
<th>Investments costs:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryogenic drying</td>
<td>1,228,400</td>
</tr>
<tr>
<td>Drying after flash</td>
<td>756,700</td>
</tr>
<tr>
<td>Conveyor dryer</td>
<td>3,213,200</td>
</tr>
</tbody>
</table>

Table 5.8
5.6.2 Investments Costs

In Appendix A.5.XXII a detailed survey of all investment costs is given. For the cryogenic option some investments cost are unknown because it is still an experimental procedure. In Table 5.8 the total investment costs per option are given.

It appears that the option of drying after the flash is the best option.
Literature


7. S. Shokansanj, D.S. Jayas, *Drying of Food Stuff*.


5.35


6 REACTION SECTION

List of Symbols

A  cross sectional area [m²]
A  area [m²]
A_c  horizontal cross section of decanter [m²]
A_s  necessary settling area [m²]
A_r  real settling area according to decanter geometry [m²]
A,B,C  Antoine constants [-]
C  concentration [Kg/m³]
d  diameter (particle, droplet) [m]
dH_c  height of coalescence layer [m]
d(t)  differential of time [h]
dP  pressure drop from figure 3 [MWK]
dP_r  real corrected pressure drop [bar]
d_{s,2}  mean sauter diameter [m]
D  agitator diameter [m]
D  decanter diameter [m]
D_h  hydraulic diameter [m]
E(-)  distribution function [1/h or 1/m]
g  gravity acceleration [m/s²]
h  holdup [-]
I  width of interface [m]
K  reaction rate [Kg/m²h]
K  K-value [-]
L  decanter length [m]
N  number of particles [-]
N  agitator speed [rpm]
N_{rel}  Reynolds number light phase in decanter [-]
N_{reh}  Reynolds number heavy phase in decanter [-]
N_3  actual mixing speed in reactor 2 (after reduction) [rpm]
P  pressure [bar]
P  power number [-]
P_{op}  operating pressure [bar]
Q  flow rate [1/h]
Q_s  volumetric flow of feed [m³/h]
Re  Reynolds number [-]
t  time [h]
t  distance from center to given chord [m]
t_d  time to pass through dispersion band [s]
T  temperature [Kelvin]
T  reactor height [m]
u_t  terminal settling velocity [m/s]
v_l  velocity through light phase outlet [m/s]
v_h  velocity through heavy phase outlet [m/s]
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reactor

\[ V \] volume \([m^3]\)
\[ V \] fraction of feed vaporised \([mole/mole]\)
\[ V_i \] volume of reactor \(i\), based on reaction kinetics \([m^3]\)
\[ V_{ir} \] volume of reactor \(i\), including vapour volume \([m^3]\)
\[ x \] mole fraction in liquid phase [-]
\[ y \] mole fraction in vapour phase [-]
\[ z \] mole fraction in feed [-]
\[ Z \] reactor diameter \([m]\)

Greek symbols

\[ \theta_c \] coalescence time \([s]\)
\[ \rho \] density \([kg/m^3]\)
\[ \rho_p \] density difference \([kg/m^3]\)
\[ \tau \] (average) residence time in reactor \([h]\)
\[ \Phi \] flow rate \([l/h]\)
\[ \eta \] viscosity \([Pas]\)
\[ \varepsilon \] power per unit mass (in reactor 2) \([J/kgs]\)
\[ \sigma \] surface tension \([N/m]\)

Subscripts

\[ p \] particle
\[ s \] surface
\[ f \] filter
\[ o \] out, leaving reactor
\[ t \] tube
\[ v \] volumetric
\[ av,o \] average leaving reactor
\[ c \] CSTR
\[ i \] of component \(i\)
\[ 1 \] of reactor 1
\[ 2 \] of reactor 2
\[ c \] of continuous phase
\[ d \] of dispersed phase
\[ mix \] of mixture
\[ m \] of mass
\[ l \] (alloted to) light phase
\[ h \] (alloted to) heavy phase
\[ min \] minumum
\[ ol \] outlet light phase
\[ oh \] outlet heavy phase

Superscript

\[ sat \] saturation condition
Summary

The goal of the reaction section is chemical breakdown of 1000 kg/h PU and partial work-up of the product-streams. The chemical breakdown occurs in two reactors in series with a filter between the reactors. The volume of the first reactor is 22.6 m$^3$ and the diameter is 2.57 m. The volume of the second reactor is 21.6 m$^3$ and the diameter is 2.04 m. The operation pressure in both reactors is 3 bar and the operation temperature in both vessels is 200 °C. The total costs of the two reactors including isolation, the filter and the pump between the two reactors is estimated at approximately fl. 183,000.

The product-stream contains two liquid phases namely a rigid and a flexible phase of respectively 10150 kg/h and 850 kg/h. These phases are separated in a settler. The volume of the settler is 0.51 m$^3$. The diameter of the settler is 0.51 m. The operation pressure is 2 bar and the operation temperature is 200 °C. The total costs are approximately fl. 8,000.

MEG is separated from the rigid stream by distillation. The purified rigid phase flow leaving the bottom of the column is 381 kg/h.

In this case two types of columns can be used namely a sieve plate column and a packed column. The volumes are respectively 17.2 m$^3$ and 10.9 m$^3$. The diameters are 1.48 m and 1.35 m. The total costs are fl. 161,250 and fl. 130,100.
6.1 Introduction

The goal of the reaction section is chemical breakdown of PU-particles into Rigid and flexibles. The breakdown takes place in a reactor. As a result of this breakdown a two phase system occurs namely the rigid and flexible phase. These phases will be separated in a settler. The flexible phase will be led to the extractor. In order to partly purify the rigid phase from MEG a distillation column is needed. So the reaction section consists of a reactor, a settler and a distillation column.
6.2 Reactor design

In the reactor, PU (poly-urethane) particles from the feed section break down by to flexibles (polyol chains) and rigids, by glycolysis with mono ethylene glycol (MEG) in the main reaction, and di-amino-diphenylmethane (DADPM) and CO₂ by hydrolysis in a side reaction. The main reaction is catalysed by potassiumacetate (KAc), in order to prevent the occurrence of other side reactions. The KAc will be dissolved in MEG. In the reactor exists a four phase system: liquid flexibles-MEG and rigids -MEG phases, solid PU, and a vapour phase containing mainly CO₂ and MEG. Because of this multi phase behaviour, special attention is needed for agitation. Requirements for the feed of the settler are satisfied in the reactor.

In the reactor effluent there must be little particles with a diameter larger than that of a PU molecule to avoid downstream contamination of the plant.

The chemical breakdown of PU particles is described with a 'shrinking particle' model. Kinetic data are derived from batch data of ICI experiments.

The operation pressure in the reactor must be such that there is a minimum risk of MEG explosions and a minimum loss of MEG by vaporisation. Because of a constant production of CO₂ a constant vent of vapour from the reactor is required in order to avoid pressure build-up.

The reactor will be very complex in practice. In this stage of the design ideal phase and reactor behaviour is assumed. In a later stage of the design the results may be used as a basis for more rigorous calculations.
6.3 Kinetic Model

6.3.1 Reactions

PU breaks down by two reactions:

\[ \text{PU} + \text{MEG} \rightarrow \text{flexibles} + \text{rigids} \] \hspace{1cm} (A)

\[ \text{PU} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{flexibles} + \text{DADPM} \] \hspace{1cm} (B)

See appendix A6.I for structure formula's.

The glycolysis (A) is the main reaction and occurs at about 200°C. The hydrolysis (B) is an unpleasant side reaction, occurring above 160°C. Poisonous DADPM is produced. The hydrolysis can only be suppressed by reducing the amount of water in the feed.

6.3.2 Kinetic Model

PU enters the reactor as particles with a diameter \( d_0 \), assumed to be equal for all particles. The reaction is assumed to occur only at the particle surface, until the particle diameter, \( d_p \), is 0. Even though this assumption is not correct, at a certain point the PU particle will be 'dissolved' in the MEG, it is safe. Reaction rate of a dissolved molecule will be larger than that of a particle, so a calculated reactor volume will be oversized, leading to a deeper conversion than calculated.

The feed is a slurry of PU particles in MEG. For this reason and because downstream contamination is best controlled by assuring an effluent with no particles or with only particles at molecule diameter or smaller, the reaction kinetics are described with the shrinking particle model. This leads to the particle diameter as a function of reaction time.

The basis of this model is a mass balance for a PU particle:

decrease of PU particle mass in time = reaction of PU.
The reaction is assumed to occur only at the particle's surface, and to be first order in PU and in MEG. Because there is a surplus of MEG at the particles surface the reaction is pseudo first order in PU. No diffusion limitation of reactants or products is taken into account.

Now the mass balance can be written as:

$$\frac{d(PU)}{dt} = - K_s C_m A_p(t)$$  \hspace{1cm} (6.1)

in which  
- PU = particle mass  
- $K_s$ = surface reaction rate constant  
- $C_m$ = concentration MEG at surface  
- $A_p(t)$ = particle surface in time.

Equation 6.1 can be combined with the well known equations for volume and surface of a sphere:

$$V_p = \frac{1}{6} \pi d_p^3$$  \hspace{1cm} (6.2)

$$A_p = \pi d_p^2$$  \hspace{1cm} (6.3)

in which:  
- $V_p$ = particle volume  
- $d_p$ = particle diameter  
- $A_p$ = surface area of sphere

The differential equation can be solved, and contracting $K_s$ and $C_m$ to $K_0$ (assuming $C_m$ to be constant) yields:

$$d_p(t) = d_{p,0} - \frac{2 K_0}{\rho} t$$  \hspace{1cm} (6.4)

in which $\rho$ is the density of solid PU with porosity 0. The complete derivation of equation 6.4 is shown in appendix A6.II. Note that mathematically $d_p$ can drop to values lower than zero!

Equation 6.4 is used to calculate $K_0$ (see appendix A6.III). At 197°C $K_0$=0.092 (Kg$_{PU}$/h m$^2$$_{PU}$). The reaction temperature must be as high as possible to assure a maximum $K_0$. 

6.7
figure 6.1: Reactor system in practice

figure 6.2: Model of the first real reactor
6.4 Modelling the Reactor and it’s Performance

6.4.1 The Reactor Model

As mentioned, a maximum diameter of the particles leaving the reactor has to be assured. This can be accomplished by placing a filter at the end of the reactor. Only particles with a diameter smaller than that of the filter perforations \(d_f\) can leave the reactor.

The reactor(s) in practice will be tank(s), because operation of a tube is difficult, due to the multi-phase character of the fluid, production of CO\(_2\) and vaporisation of MEG. To create a homogeneous fluid stirred tanks are needed. A second tank reactor is added in series for further PU breakdown. In practice there will be two tank reactors in series, the first reactor will have a filter in front of it’s effluent pipe (figure 6.1).

In the model that is created, ideal behaviour is assumed for convenience.

A particle entering with \(d_p=d_0\) stays in the first reactor at least until \(d_p=d_r\). Then the particle can leave the reactor at any time, according with the residence time distribution (RTD) of an ideal tank. The RTD of particles is that of volume elements in a tank reactor. This leads to a model for the first real reactor: an ideal tube assuring minimum particle residence time, followed by an ideal tank assuring particle residence time distribution (figure 6.2). A residence time distribution function, \(E(t)\), for this model of the first real reactor is shown in figure 6.3.

Adding a second tank in practice, means that a tank has to be added to the model too (figure 6.4). A typical \(E(t)\) for such a system is shown in figure 6.5. The reactor system in practice will have such a RTD.

6.4.2 Overall Performance of Items in the Model

The performance calculations are derived from ideal tube and CSTR behaviour on basis of reduction of particle diameter. Diameter reduction can always be converted to reduction of mass by:

\[
\text{conversion of mass} = \xi = \frac{d^3_{\text{feed}} - d^3_{\text{out}}}{d^3_{\text{feed}}} \quad (6.5)
\]
Figure 6.3: Typical RTD curve for the first real tank

Figure 6.4: Model for the complete reactor system
6.4.2.1 Performance of an Ideal Tube

Particle's moving through a tube have only one residence time, and thus a specific time to react. So the performance of a tube is similar to equation 6.4 thus:

\[ d_{p,o} = d_0 - \frac{2 K_0 \tau_t}{\rho} \]

\[ \tau_t = \frac{V_f}{\phi_v} \]  

in which:
- \( d_{p,o} \) = diameter of particle leaving tube
- \( d_0 \) = diameter of particle entering tube
- \( \tau_t \) = residence time in tube
- \( V_f \) = tube volume
- \( \phi_v \) = feed volume flow.

6.4.2.2 Overall Performance of a CSTR

The performance of a tank is derived on a mass balance basis. Because we can only speak of an average residence time, we can only speak of an average diameter of the particles leaving the reactor.

The mass balance can be written as:

PU mass leaving = PU mass entering - PU mass converted (kg/h)

Mathematically:

\[ \dot{\phi}_{m,o} = \dot{\phi}_{m,i} - K_0 A_p N \]  

in which: \( N \) = number of particles in the tank.

Combining 7 with a particle flux, and the relation linking mass and diameter of a particle yields (see appendix A6.IV):

\[ d_{av,o}^3 = d_0^3 - \frac{6 K_0 \tau_c}{\rho} d_{av,o}^2 \]

in which:
- \( d_{av,o} \) = average diameter in/leaving the CSTR
- \( d_0 \) = diameter of particles entering reactor
- \( \tau_c \) = average residence time in CSTR

The diameter of leaving particles is a mass average. Equation 6.8 can be used to calculate the conversion in a CSTR, without regarding the particle size distribution of the effluent, or the amount of particles.
6.4.3 Particle Size Distributions in the Reactor Model

6.4.3.1 Introduction

Because the particles do not all have the same residence time in a tank, the particles in a tank’s effluent will not all have the same diameter, but a particle size distribution (PSD) will occur.

Downstream contamination is determined by the amount of particles leaving the reactor and their diameter’s. The design requirement to minimize contamination is:

'' in the effluent the fraction of particles having a diameter larger than a certain maximum, must be small''

To determine reactor volumes that live up to this requirement the particle size distributions in the effluent streams as a function of the reactor volumes (or residence times) must be known.

In the following calculations, a uniform feed of PU particles is assumed.

6.4.3.2 PSD of an Ideal Tube

As there is only one residence time in an ideal tube, there is only one particle diameter leaving the tube. The diameter size can be calculated with equation 6.6.

6.4.3.3 PSD of a CSTR

The residence time distribution function of an ideal tank with average residence time \( \tau = \frac{V_i}{\Phi} \), is:

\[
E_1(t) = \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right)
\]  

(6.9)

The fraction of volume elements with a residence time between \( t_1 \) and \( t_2 \) is:

\[
F(t_1 < t < t_2) = \int_{t_1}^{t_2} E_1(t) \, dt
\]  

(6.10)

In order to derive the particle size distribution, \( t \) and \( d(t) \) (the differential of \( t \)) must be eliminated from equation 6.9.

First (4) is rewritten to:

\[
t = \frac{(d_p - d_0) \rho}{2 K_0}
\]  

(6.11)
Figure 6.5: Typical RTD curve of complete model (two real tanks in series)

Figure 6.6: PSD curves for a one tank (a) and a two tank (b) system
and $d(t)$ is derived from (11):

$$d(t) = \frac{-\rho}{2} d(d_p)$$  \hspace{1cm} (6.12)

After elimination of $t$ and $d(t)$, the particle size distribution must be normalised by stating:

$$F(-\infty<d_p<d_0) = \int_{-\infty}^{d_0} E_1(d_p) \, d(d_p) = 1$$  \hspace{1cm} (6.13)

For mathematical reasons the lower boundary must be -inf., and not 0. This yields the particle size distribution in the effluent of an ideal tank:

$$E_1(d_p) = \frac{A}{\tau} EXP\left(\frac{-A}{\tau} (d_0-d_p)\right)$$  \hspace{1cm} (6.14)

$$A = \frac{\rho}{2} K_0$$

See appendix A6.V for a the derivation. The curve of equation 6.14 for $A=500$ and $\tau=10$ is shown in figure 6.6a.

6.4.3.4 PSD of Two CSTR's in Series

Because the residence time distribution of two tanks gives rise to less particles with a short residence time, and thus less particles with a large diameter in the effluent two tanks in series is also an interesting case for our purposes.

Two cases must be regarded: two tanks with equal volume's and two with different volumes.

6.4.3.4.1 Two CSTR's with equal volumes.

The $E(t)$ function for this case is:

$$E_2(t) = \frac{t}{\tau^2} EXP\left(-\frac{t}{\tau}\right)$$  \hspace{1cm} (6.15)

Eliminating $t$ with equation 6.11, and normalising (see appendix A6.VI) yields the PSD function:

$$E_2(d_p) = \left(\frac{A}{\tau}\right)^2 (d_0-d_p) EXP\left(\frac{-A}{\tau} (d_0-d_p)\right)$$  \hspace{1cm} (6.16)
### 6.4.3.4.2 Two CSTR's with different volumes.

First the $E(t)$ function of the two tanks has to be derived. These calculations are expanded on in appendix A6.VII. The result is:

$$E_2(t) = \frac{1}{\tau_1 - \tau_2} (\exp(-\frac{t}{\tau_1}) - \exp(-\frac{t}{\tau_2})) \quad (6.17)$$

By eliminating $t$ and $d(t)$, and next normalizing, see appendix A6.VIII, the particle size distribution function is derived:

$$E_2(d) = \left(\frac{A}{\tau_1 - \tau_2}\right) \left(\exp\left(-\frac{A}{\tau_1}(d_0 - d)ight) - \exp\left(-\frac{A}{\tau_2}(d_0 - d)\right)\right)$$

$$A = \frac{p}{2K_0} \quad (6.18)$$

The fraction of particles of the feed with a diameter between $d_1$ and $d_2$ in the effluent is:

$$F(d_2 < d_p < d_1) = \int_{d_2}^{d_1} E_2(d_p) \, d(d_p) \quad (6.19)$$

This counts for both the equal and unequal tanks case. A general curve for equation 6.18 is figure 6.6b ($A=500$, $\tau_1=5$, $\tau_2=5$)

### 6.5 Characteristics of the Model's Performance

The character of the model is studied by plots of particle size distribution functions 16 (two tanks with same volume) and 18 (two different volumes).

A typical PSD curve for a two tank system is plotted in figure 6.6b. Note that the maximum diameter of a particle in the effluent is $d_1$. This is the diameter of the particles entering the two tank system of the model, thus the diameter of particles leaving the tube in the model. In practice the diameter of the particles at filter perforation diameter.

We are interested in a high performance leading to a small number of large particles in the effluent. In figure 6.6b this means that from $d_0$ downwards to 0, $E(d_p)$ must have low values, resulting in a small surface under the curve, and thus a small fraction of large particles in the effluent.
figure 6.7: PSD curves at different values of 'A'

figure 6.8: 'two' PSD curves of two unequal tanks in different order
A (large) part of the figure is drawn on the negative \( d_p \) axis. Negative \( d_p \)'s are only mathematically relevant. The surface under the curve, left to the \( E(d_p) \) axis, is the fraction of the particles entering the reactor system that will react totally in the reactor. Thus the surface right to the \( E(d_p) \) axis is the fraction of not totally reacted particles.

Figure 6.7 shows how the distribution changes if \( A \) in equation 6.17 is enlarged (or \( K_0 \) is reduced). Lower \( K_0 \) leads to a worse distributions and lower conversion of PU.

Figure 6.8 shows that for a certain \( \tau_1 \) and \( \tau_2 \) the order of tank volumes does not influence the performance. In other words: the order of two tanks with different volumes does not influence the performance. This can also be concluded by looking at equation 6.18 carefully.

Figure 6.9 shows that for a certain total \( \tau \) (here 7 h) the distribution of residence time across tank 1 and 2 influences the performance. Case 1 and 2 are plotted with equation 6.18, Case 3 with equation 6.16. From this figure it can be concluded that two equal tanks have the best performance. Thus for a certain required performance two equal tanks in series will be most efficient, as the total reactor volume is at it's minimum.

A certain performance can theoretically also be accomplished by omitting the second tank. This leads to a very large volume of the remaining tank. This is not efficient at all.

So as far as conversion is concerned, two equal tanks is in practice the cheapest option.

### 6.6 Determination of the Real Reactor Volumes

What happens in practice is difficult to reason. Particles entering real tank 1, will stay there at least until their diameter is reduced enough to pass the filter. Particles larger than \( d_r \) can not leave the reactor, but the MEG can so there is no build up of volume in the tank. In a steady state the number of particles entering is as big as the number of particles reaching the filter diameter \( d_r \). So there are \( N \) particles (\( N = \text{particle flux entering} \times \text{time required to react from entering diameter to filter perforation diameter} \)) larger than \( d_r \) in the tank.

After reaching \( d_r \), particles may leave or stay in the reactor. So, next to the particles bigger than \( d_r \), there will be particles smaller than \( d_r \). The residence time of particles, and thus the conversion of PU particles smaller than \( d_r \) is controlled by the tank volume.
Figure 6.9: Three cases of distribution of $\tau$ across two tanks.
The number of particles in the reactor, smaller than \( d_r \) can be calculated for a certain tank volume (or residence time):

\[
N(d_p<d_r) = \text{particle-flux of feed} \times \tau_{\text{tank}} \times \text{fraction}(d_p>0) \tag{6.20}
\]

The fraction is calculated by integrating equation 6.13:

\[
\text{fraction}(d_p>0) = \int_0^{d_r} E_1(d_p) \ d(d_p) \tag{6.21}
\]

So the total amount of particles in the first real tank can be calculated.

Theoretically the number of particles in the first real tank in a steady state can be so large that the entire volume is taken by PU. This occurs if the volume of total PU particles smaller than \( d_r \) in the reactor is too large due to filter contamination. Or the tank volume is as big as or smaller than the total volume of particles larger than \( d_r \) in the reactor.

From the above mentioned it can be concluded that the volume of the tube in the model of the first real reactor is of minor interest for the real volume of the first tank. In fact tank volumes calculated with the model, (resulting from a certain chosen requirement) will be the volumes of the two tanks in practice.

Two tanks of equal volume in series will be used in practice (the first with a filter in its effluent pipe). The procedure for calculation of the real tank volumes is:

1. Choose a filter diameter \( d_r \),
2. Choose a fraction of particles in the effluent with 'lower-boundary' \( d_p \) < \( d_r \),
3. Combine equations 6.16 and 6.19, and solve,
4. This yields the \( \tau \), and thus volumes of tank 1 and 2.

Note that reactor volume in the above and the below must be read as the volume of the reacting liquid. The reactors in practice will be larger due to considerations other than reaction kinetics. This will be discussed further on.
6.7 Calculating with the Model

6.7.1 Method

The particles coming from the feed section are assumed to have a uniform diameter of 5e-4 m. This is \( d_0 \) in equation 6.5. In case the particles are not uniform distributed, the average diameter have to be calculated. \( D_0 \) then becomes the average diameter, this doesn’t influence the reliability of the model.

Because the perforation diameter of the filter in the real reactor, has a minimum value of 5e-5 m (due to pressure drop across the filter), this is chosen as \( d_{p,o} \) in equation 6.6, from which the tube residence time can be calculated.

For reactor volume calculations \( \tau \) and volume flow are required. The volume flow is assumed to be constant and 10 m\(^3\), see appendix A6.IX.

The molecule diameter of PU is according to calculations of dr.ir. K. ten Nijenhuis (TU-Delft, 7-11-1991) 5 to 10 nm (5e-9, 1e-8 nm). The design requirement for the total reactor is chosen to be:

'the fraction of particles leaving the reactor with a diameter between 5e-5 (filter perforation diameter, \( d_p \)) and 1e-8 must be 0.01 (or smaller)'.

Mathematically this means, integrating equation 6.16 (the most efficient two equal tanks case):

\[
0.01 = \int_{1e-8}^{d_p} E_2(d_p) \, d(d_p)
\]

This equation can be solved analytically (see appendix A6.X):

\[
0.01 = \frac{A \, d_p}{\tau} \left( 1 - EXP\left( \frac{A}{\tau} (10^{-8} - d_p) \right) \right) - \left( \frac{A}{\tau} d_p-1 \right) + EXP\left( \frac{A}{\tau} (10^{-8} - d_p) \right) \left( \frac{A}{\tau} 10^{-8} - 1 \right)
\]

Solving equation 6.23 yields the \( \tau \) of the two tanks. This is converted to volume with:

\[
\tau = \frac{\text{tank volume}}{\text{feed volume flow}}
\]

Equation 6.23 has been solved with MERCURY, a numerical equation solving program. The relevant file is shown in appendix A6.XI.
6.7.2 Results

The results of the calculations are:

1. A tank volume (reacting liquid) 20 m³ for both tanks.
2. \( t = 2.0 \) h. for both tanks.
3. Average diameter of particle leaving first reactor = 1.1e-5 m.
4. Conversion in first tank = 99.999%, in the second tank 0.001%

It can be proven that the volume occupied by PU-particles in the reactor is about 1 vol% (see appendix A6.XII). This means that there is no danger of overflow in the reactor.

6.8 Operation Pressure and Temperature

6.8.1 Introduction

Operation of the reactors must yield sufficient conversion, and on the other hand operation must be safe.

To assure the conversion needed, the temperature must be as high as possible. A high temperature can be unsafe eg. because of vaporisation of explosive MEG. The vaporisation of MEG, and the concentration of MEG in the vapour can be controlled by choosing a sensible operation pressure.

6.8.2 Operation Temperature

All performance calculations are done with a reaction rate constant at +/- 200°C., because no other information was provided. However it is poor, it is obvious to maintain that temperature for this reason.

6.8.3 Operation Pressure

6.8.3.1 Introduction

The pressure in the reactor must be such that there is not too much MEG vaporisation, and the concentration of MEG in the vapour is not too high.

Determination of an operation pressure roughly is done by performing a flash calculation for the reaction mixture. Only MEG, CO₂ and DADPM are taken into account: flexibles and rigid are omitted. It is assumed they contribute little to the phase behaviour of three other components.
The flash calculation is taken from Smith [1]. It assumes ideal phase behaviour.

MEG concentration in the vapour can be controlled by adding inerts. Here the CO$_2$ produced is such. Because conversion in the first tank is about 100%, no CO$_2$ is released in the second. This calls for a special solution for tank 2.

### 6.8.3.2 Flash Calculation Handling

The flash calculation is done with the mixture in the first reactor. Because conversion is about 100%, all CO$_2$ and DADPM (and the omitted flexibles and rigidis) is produced in the first reactor. This mixture of CO$_2$, DADPM together with MEG is the feed for the calculation. So the next calculation are for the first reactor.

We are interested in the fraction of the feed vaporised (V), and the composition of vapour and liquid at different pressures, so the 'best' pressure can be chosen. Therefore the following equations must be solved:

V is calculated by solving:

$$\sum_{i} \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \quad (6.25)$$

in which: $z_i =$ mole fraction of component i in the feed

and:

$$K_i = \frac{x_i}{y_i} = \frac{P_i^{sat}}{P} \quad (6.26)$$

in which: $x_i =$ mole fraction of component i in liquid phase

$y_i =$ mole fraction of component i in vapour phase.

Mole fractions of the individual components can be calculated by combining equation 6.26 with:

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \quad (6.27)$$

The values of $P_i^{sat}$ are temperature dependant, and can be calculated (at 200°C in this case) with equations like:

$$\ln(P_i^{sat}) = A - \frac{B}{T - C} \quad (6.28)$$

in which: $T =$ temperature

$A, B, C$ are component dependant constants.
**Table 1: Results of the Flash Calculations for the Reactor**

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Vapour Mole Fraction</th>
<th>y(DADPM)</th>
<th>y(CO2)</th>
<th>y(MEG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.98705</td>
<td>2.1267 e-4</td>
<td>2.0078 e-3</td>
<td>0.99818</td>
</tr>
<tr>
<td>1.5</td>
<td>7.244 e-3</td>
<td>2.3475 e-6</td>
<td>0.26904</td>
<td>0.73124</td>
</tr>
<tr>
<td>2.0</td>
<td>4.225 e-3</td>
<td>1.7554 e-6</td>
<td>0.45162</td>
<td>0.54841</td>
</tr>
<tr>
<td>3.0</td>
<td>2.877 e-3</td>
<td>1.1687 e-6</td>
<td>0.63474</td>
<td>0.36558</td>
</tr>
<tr>
<td>4.0</td>
<td>2.401 e-3</td>
<td>8.7608 e-7</td>
<td>0.72635</td>
<td>0.27416</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>x(DADPM)</th>
<th>x(CO2)</th>
<th>x(MEG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>60.28 e-4</td>
<td>0.016 e-5</td>
<td>0.90910</td>
</tr>
<tr>
<td>1.5</td>
<td>9.981 e-4</td>
<td>3.307 e-5</td>
<td>0.99896</td>
</tr>
<tr>
<td>2.0</td>
<td>9.951 e-4</td>
<td>7.402 e-5</td>
<td>0.99893</td>
</tr>
<tr>
<td>3.0</td>
<td>9.938 e-4</td>
<td>1.560 e-4</td>
<td>0.99885</td>
</tr>
<tr>
<td>4.0</td>
<td>9.933 e-4</td>
<td>9.933 e-4</td>
<td>0.99877</td>
</tr>
</tbody>
</table>
6.8.3.3 Calculations and Results for the First Reactor

Assuming about 0.5% water in the feed, the mole-fractions for the flash calculation will be (appendix A6.XIII):

\[
\begin{align*}
    z_c &= 0.001982 \text{ (CO}_2\text{)} \\
    z_d &= 0.000991 \text{ (DADPM)} \\
    z_m &= 0.997027 \text{ (MEG)}
\end{align*}
\]

For certain P-values, K-values for all components are calculated (equations 6.26 and 6.28) so vapour fraction could be calculated at different pressures (Table 6.1). So at different pressures vapour compositions can be calculated (equation 6.27), see Table 6.2. Calculations are performed by MathCad, appendix A6.XIV.

Table 6.2 shows a small MEG concentration in the vapour, at 3 bar. The mole fraction of reactor feed vaporised is small: 0.00288. Operation pressure is chosen to be 3 bar, as it is a 'low' pressure, resulting in little vaporisation and low MEG concentration in the vapour.

As the total mole flux entering the reactor flash is 162.5 kmol/h (MEG, CO\textsubscript{2}, DADPM) 10.6 kg/h MEG will be vaporised. The amount of CO\textsubscript{2} released into the vapour phase is 13.65 kg/h, the amount of DADPM vaporising is 0.001 kg/h.

6.8.4 The Second Reactor, Operation in Practice

Because conversion in the first reactor is about 100%, the liquid phase of the first and the second reactor will be more or less the same. It also means that almost no CO\textsubscript{2} is produced in the second tank. When operating at 200°C MEG will freely vaporise, and the vapour phase contains about 100% MEG.

To avoid this pressure have to be built up by adding inert gases. A cheap solution is to feed the vapour of the first reactor to the second. The same equilibrium, thus the same operation pressure, as in the first tank will be achieved because, as mentioned, the liquid phase in tank 1 and 2 are almost equal, and the vapour phases too (in case the vapour is fed through).

High pressure in the reactor can be achieved by letting the vapour build up to 3 bar at the start up of the plant, and venting vapour as soon as the pressure becomes too high.
6.9 The Reactor Hardware

6.9.1 Introduction

Once the reactor has been designed on the basis of the chemical kinetics, the actual construction has to be designed. In this case there are two agitated vessels meaning that a choice concerning the actual mixers has to be made. The mathematical model is based on a filter being present between the two reactors, a way to realize this in practice has to be designed. Since there will be CO₂-development mainly in the first reactor, and vaporisation of MEG in both, it has to be figured out what to do with these vapour streams. For a representation of the reactor hardware the reader is referred to figure 6.10. As soon as all hardware is known, a cost analysis of the reactor can be made.

6.9.2 The First Reactor

The reactor-influent coming from the feed section is a liquid mixture with a temperature of 200°C. At an operation pressure of 3 bar it should be possible to use standard measurements for the geometry, this results in a height of 1.5 times the vessel diameter. Once the geometry has been set a calculation can be made to check if the mixture is turbulent enough to assure homogenous mixing. In order to achieve good axial as well as radial mixing a propeller is used with a diameter of 1/3 times the diameter of the vessel. To improve mixing four baffles can be added. To check on turbulence, the Reynolds number must be calculated using the following equation [2]:

\[
Re = \frac{N D^2 \rho}{\eta}
\]  

(6.29)

in which:

- \(N\) = agitator speed in rotations per second
- \(\rho\) = density of mixture at given temperature
- \(\eta\) = viscosity of mixture at given temperature
- \(D\) = diameter of the agitator

If the calculated Reynolds number is larger than \(10^4\) it means that the flow is turbulent [3].

Results of the design so far are:

- \(N_1 = 95\) rpm
- vessel-diameter = 2.6 m
- vessel-height = 4 m
- agitator-diameter = 0.86 m

The calculated vessel-height is based only on liquid volume. To leave space for the vapour phase 0.5 m can be added. This does not influence \(Re\).
A vessel thickness of 9 mm under these conditions is on the safe side. For the complete design calculation of the first reactor the reader is referred to appendix A6.XV.

6.9.3 The Filter System

Because of kinetic considerations a filter is placed between the first and the second reactor. Reactor volumes are based on a model with filter perforations of 5.0e-5 m.

Because of the fact that the reactor system must be able to operate continuously, two filters must be applied in series. This filter system operates as follows (see figure 6.10). When the pressure drop over filter 1 reaches a value implicating that insufficient filtering is taking place, the concerning filter is shut down and filter 2 is put in operation. This can be realized quite simple with a pressure controller measuring the pressure over the pump installed between the first and the second reactor.

Once the filter system has been designed, the actual filters and corresponding pressure drop have to be determined. Based on data off existing filters, supplied by Amafilter b.v. [6], (see appendix A6.XV) it has been found that wedge-wire basket filters would suffice. From the supplied data it can be concluded that a filter type 72-S-I with 325 mesh wedge-wire, corresponding with a filter diameter of 5e-5 m would perform as required. Once the filter is chosen the corresponding pressure drop can be determined from data by Amafilter. At a flowrate of 10 m³/h and a pressure drop of 0.1 bar results, if a junction connecting effluent pipe and filter of 2 inches is applied. Even though the filter is placed just outside the reactor (for service reasons) no holdup of PU in the (short) pipe between first reactor and filter is expected because of high turbulence mixing in the first reactor.

When a filter is contaminated, it has to be removed and cleaned. This can be done by back flushing, or manually. Because the liquid passing the filter is assumed to be 'clean', and PU particles break down manual cleaning is best, because the 'cleaning frequency' will be low. Cleaning by backflushing is much more expensive. In case of a high 'cleaning frequency' it is preferred.

For the data on which the pressure drop is based, the reader is referred to appendix A6.XV once more.
6.9.4 The Second Reactor

Design of the second reactor is more crucial than that of the first reactor. This is because of the two requirements which have to be met:

A sufficient mixing
B Sauter diameter of the dispersion $d_{3,2} = 1\text{ mm}$

The value of 1 mm is about the smallest possible diameter because of the settling from the dispersed phase which has to take place after the second reactor. The second requirement is more important than the first because of the fact that an almost 100 percent conversion of the PU particles has taken place in the first reactor. This means that the mixture coming into the second reactor is by itself already homogenous meaning that the mixing speed is less critical, the dispersion does not have to be created, but only maintained. This implicates that an agitator can be designed based on the required Sauter diameter in the dispersion in the second reactor [4]. The formula determining the Sauter diameter in an agitated vessel with measurement other than standard is [3]:

$$d_{3,2} = 0.11 \left( \frac{\sigma^{0.6}}{\varepsilon^{0.4} \rho_c^{0.6}} \right)^{h^{0.5}} \left[ \frac{\eta_d}{\eta_c} \right]^{0.25}$$  \hspace{1cm} (6.30)

in which:
- $d_{3,2}$ = Sauter diameter
- $\sigma$ = surface tension
- $\varepsilon$ = dissipated energy per unit mass
- $\eta_{dc}$ = viscosity of dispersed/continuous phase
- $\rho_c$ = density continuous phase
- $h$ = hold up

Measurements of the vessel are linked to $\varepsilon$ by:

$$\varepsilon = \frac{P_v \rho N^3 D^5}{\rho \left( \frac{\pi}{4} T^2 Z \right)}$$  \hspace{1cm} (6.31)

in which:
- $P_v$ = power number
- $N$ = number of resolutions of direct drive
- $D$ = agitator diameter
- $T$ = vessel diameter
- $Z$ = vessel height

The best results are found with a vessel height of 3 times the vessel diameter and a turbine diameter of 1/4 times the vessel diameter [5]. These are no standard measurements meaning that it is necessary to place two turbine-agitators in line in order to get sufficient mixing performance. Here turbine agitators are used because they are less expensive than propellers and axial mixing is not critical like in the first reactor. When a standard direct drive is used, the resulting agitator speed is 6.21
much too high. In order to realize a speed necessary for the required dispersion a reduction of the number of revolutions will have to be applied. For the complete calculation based on the required sauter diameter the reader is referred to appendix A6.XV. The results are:

\[
\begin{align*}
N_{\text{direct}} &= 129 \text{ rpm} \\
N_{\text{agitator}} &= 9 \text{ rpm} \\
D_2 &= 0.51 \text{ m} \\
T_2 &= 2.1 \text{ m} \\
Z_1 &= 6.1 \text{ m}
\end{align*}
\]

Again the volume is based only on the liquid volume, and again 0.5 m can be added in height for the vapour phase.

There remains one point in the reactor design and that is the CO₂ development which occurs mainly in the first reactor. These vapour streams, which also include some MEG vapour have to be removed. In order to realize this the following system has been thought of. The CO₂-MEG vapour from the first reactor is led to the second reactor where it in turn is purged towards a condenser where the MEG is condensed to liquid. The CO₂ is led to storage. A demister pad placed at the CO₂ outlet of the condenser has to make sure that no MEG goes with the CO₂. The MEG stream, being very small, is led back to the second reactor.

This completes the design of the reactor.

### 6.10 Cost Estimation

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost (fl.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor 1 (mixing vessel)</td>
<td>73,000</td>
</tr>
<tr>
<td>Isolation reactor 1</td>
<td>12,650</td>
</tr>
<tr>
<td>Reactor 2 (mixing vessel)</td>
<td>78,000</td>
</tr>
<tr>
<td>Isolation reactor 2</td>
<td>8,350</td>
</tr>
<tr>
<td>Filter system (72-S-I)</td>
<td>9,500</td>
</tr>
<tr>
<td>Pump</td>
<td>1,700</td>
</tr>
<tr>
<td><strong>Total costs</strong></td>
<td><strong>183,200</strong></td>
</tr>
</tbody>
</table>

The cost calculation can be found in volume II.
6.11 Conclusions and Recommendations

The reaction-system is definitely oversized. This has to do with the fact that the homogenous breakdown of PU in the second reactor has not been taken into account. For this part of the reaction the "shrinking particle" model is also used; this leads to lower conversion-rates than in reality. The presence of a filter between the first and second reactor assures a minimum residence time of PU-particles. In this case the diameter of the filter perforations is 0.05 mm. This results in a pressure drop over the filter of 0.1 bar. Because this pressure drop is small it is possible to use an even smaller diameter of the filter perforations, which leads to a better performance of the reaction-system and thus smaller vessels. Also the rise of temperature has an advantageous influence on the performance. By rising the temperature the value of $k_o$ increases, which leads to a higher conversion-rate.

By chaining more reactors in series the same performance with a smaller volume can be reached. However, this doesn't lead to a cheaper process, the investment costs of a reaction-system with more reactors in series increases, whereas maintenance becomes more difficult. Energy costs do not rise if more tanks are used, because the process doesn't require energy input.

In modelling the reactor ideal behaviour is assumed. In reality this is not the case due to multi-phase behaviour, non ideal mixing, etc. Therefore it's essential to determine the real residence time distribution based on experiments on a pilot reactor-system.

In order to avoid explosion caused by MEG the reaction is carried out by 3 bar. In the reactor influent the ratio between PU and MEG is 10 mass%. This is however out of a chemical point of view not necessary. But decreasing the PU/MEG ratio gives rise to transportation problems of PU-particles into the reactor, which means that the reaction cannot be carried out continuously. On the other hand a decrease of the total amount of MEG implies a decrease in the size and energy-consumption of separators throughout the entire process. Therefore discontinuous operation of the reactor is probably a much cheaper than the continuous operation. It should be noticed that changing the PU/MEG ratio can change the reaction kinetics, because the reaction can become diffusion-limited.
<table>
<thead>
<tr>
<th>$\theta$</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt; 0.3$</td>
<td>Light phase always dispersed</td>
</tr>
<tr>
<td>$0.3-0.5$</td>
<td>Light phase probably dispersed*</td>
</tr>
<tr>
<td>$0.5-2.0$</td>
<td>Phase inversion probable, design for worst case</td>
</tr>
<tr>
<td>$2.0-3.3$</td>
<td>Heavy phase probably dispersed*</td>
</tr>
<tr>
<td>$&gt; 3.3$</td>
<td>Heavy phase always dispersed</td>
</tr>
</tbody>
</table>
6.12 Separation of Dispersion out of the Second Reactor

6.12.1 Composition of the Feed and Description of the Separation Problem

The dispersion coming out of the reactor consists of the following two phases which have to be separated:

- phase 1 with a mass flow rate of 850 kg/h has the following composition:
  * 714.0 kg/h Flexibles
  * 127.5 kg/h MEG
  * 8.5 kg/h DADPM

- phase 2 with a mass flow rate of 10150 kg/h has the following composition:
  * 9756.2 kg/h MEG
  * 350.8 kg/h Rigidis
  * 23.0 kg/h DADPM
  * 20.0 kg/h KAc

To determine which one of the two phases is the disperse phase, the correlation of Selker and Sleicher [7] is used:

\[
x = \frac{Q_l}{Q_h} \left[ \frac{\rho_l}{\rho_h} \frac{\eta_h}{\eta_l} \right]^{0.3}
\]  

(6.32)

in which:

- \( Q_l \) = flow rate light phase
- \( Q_h \) = flow rate heavy phase
- \( \rho_l \) = density light phase
- \( \rho_h \) = density heavy phase
- \( \eta_l \) = viscosity light phase
- \( \eta_h \) = viscosity heavy phase

This calculation, with phase 1 being the light phase (L) and phase 2 the heavy phase (H), yields an answer of \( x = 0.16 \) which is less than 0.3. According to Selker and Sleicher this means that the light phase, which in our case is phase 1, is always the disperse phase. This information is taken from Table 6.3 [8]. Because of the difference in densities of the two phases (90 kg/m\(^3\)), a settler should suffice for separation. The calculation model used can be best represented by a mixer-settler with the mixer being the second reactor. The form of the dispersion will be determined by the mixing behaviour in the second reactor. A visual representation of the model is given in figure 6.10.
The calculation of the Sauter diameter can be found in the reactor hardware section of appendix A6.XVI [4]. For the design of a settler the following steps should be used [7]:

1. Calculate the settling velocity for droplets, in this case the light phase consists of droplets meaning that they rise instead of settle.
2. Determine the necessary settling area.
3. Estimate the time required for coalescence.
4. Check the settler size chosen for turbulence levels.
5. Specify feed and outlet geometry.

Another crucial factor in the settler calculation is the chosen temperature. This basically implies an optimization because of the place the settler takes within the process-scheme. The apparatus following the settler is a distillation column which needs its feed at a temperature of 200°C. The feed of the settler coming out of the second reactor has a temperature of 200°C. Because of the fact that the settler is a one time investment unit, it does not operate on energy and needs little or no maintenance, the operating conditions are less crucial then those of the reactor, the distillation column and the extractor. When a temperature of \( t=200^\circ C \) is used at an operating pressure of 2 bar there will be almost no vaporization of MEG or any other component. The MEG has an evaporation temperature of 190°C, this is at atmospheric pressure. With the temperature set at 200°C, heat exchangers are not necessary between the reactor and the settler as well as between the settler and the distillation column. Now that the temperature is determined, the viscosities as well as the surface tension can be determined and design of the settler can take place.

### 6.12.2 Settling Velocity and Settling Area

To determine steps one and two it basically means using the following equation [3]:

\[
U_t = \frac{g}{18 \eta_c} \frac{d^2 (\rho_d - \rho_c)}{[6.33]}
\]

in which:

\[
\begin{align*}
    u_t & = \text{settling velocity of droplets} \\
    g & = \text{specific gravity} \\
    d & = \text{droplet diameter disperse phase} \\
    \rho_d & = \text{density disperse phase} \\
    \rho_c & = \text{density continuous phase} \\
    \eta_c & = \text{viscosity continuous phase}
\end{align*}
\]

It is derived from Stokes’ law using Newton’s basic drag equation. The droplet diameter used in this equation has to be on the save side in order to make sure that all of the droplets settle and a 100 percent separation is achieved. Based on practical values it is found that with a \( d_{\min} \) of 150*10^{-6} m the calculation will be on the save
side. Once the settling velocity is found it can be used to determine the minimum necessary settling surface with the following correlation [7]:

\[ A_s > \frac{Q_c}{U_t} \]  \hspace{1cm} (6.34)

in which:
- \( A_s \) = minimum necessary settling area
- \( Q_c \) = flow rate continuous phase
- \( u_t \) = settling velocity droplets disperse phase

In order to achieve reliable performance as well as meeting the necessary criterion it is necessary to use a larger settler interface \( A_c \). This can only benefit settling performance because of the larger settling area which is hereby achieved meaning an improved overflow rate as well as improved coalescence. Because of the place of the interface level being crucial it is recommended to use a level controller. In case of calamities it should be possible to shut down either one of the outlets. A simple way to check on interface level is to place a view window at the level of the interface. The difference in phase colour indicates which one of the outlets has to be shut down. As soon as the required interface level is once again reached, the concerning outlet can be opened up again. For the complete calculation and results the reader is referred to appendix A6.XVI.

6.12.3 Coalescence and Dispersion Behaviour

The time required for the collected droplets to cross the interface often is the major limit on the size of the settler. From practice [7+9] it has been empirically determined that this time is dependent upon (1) the difference in the density of the phases, (2) the viscosity of the continues phase, (3) the viscosity inside the drop, (4) the interfacial tension, (5) the mean sauter diameter \( d_{3.2} \). The correlation derived for the coalescence time results in a value of \( \theta_c = 56 \) seconds [3]. As long as this is within the time necessary to cross the dispersion band as well as within the residence time in the settler, overflow will not occur. This means a optimisation problem in order to reach these criteria as well as the criterion for the height of the settler which has to be at least 10 times the height of the dispersion band. The volume of the settler is determined by the diameter and the length of the settler, with \( L/D = 5 \). This means finding a settler which has to satisfy the following criteria [2+7]:
- coalescence time < time to pass through dispersion band.
- time to pass through dispersion band > 2 to 5 min and < residence time.
- interface area > necessary settler area.
- height of coalescence layer < 0.1 settler height.
Keeping these criteria in mind, a settler can be designed. The results, summarized below, show that all the criteria are met.

- $u_i = 0.007 \text{ m/s}$
- $A_s = 0.35 \text{ m}^2$
- $A_c = 1.2 \text{ m}^2$
- $V_s = 0.515 \text{ m}^3$
- $D = 0.51 \text{ m}$
- $L = 2.55 \text{ m}$
- $t_s = 195 \text{ m}$
- $\theta_c = 56 \text{ s}$

The complete calculation as well as a list of declaration of variables can be found in appendix A6.XVI. A visual representation of the settler with the belonging measurements is given in figure 6.11.

6.12.4 Turbulence Check and Determination of Outlet and Feed Geometry

This settler will be a horizontal cylinder, this being for economic reasons. A horizontal settler has several times as much interfacial area as it would if it were vertical. With the settler being a horizontal cylinder the continues phase will flow perpendicularly to the settling of the droplets. This movement creates turbulence which could result in poor separation. In order to check on this turbulence, Reynolds number can best be used [2].

\[
N_{Re} = \frac{V D \rho}{\eta}
\]  

(6.35)

in which:
- $v =$ entering velocity outlet
- $D =$ outlet diameter
- $\rho =$ phase density
- $\eta =$ phase viscosity

The calculations are performed for both phases. The following guidelines pretty well summarize experience from successful settlers:
Calculation of the Reynolds number for the light phase, shown in the settler section of the appendix A6.XVI, results in a value which will give little turbulence problems. For the heavy phase a Reynolds number of a little over 20,000 is found. This could cause some hindrance. A solution for this problem can be provided by a diffuser placed a little in front of the outlet. In order to determine the diameters of the outlets as well as the inlet one must keep in mind that the velocity through these outlets can not exceed 3 m/s [5]. Knowing the throughput to be achieved, determination of the minimum necessary outlet diameter is simple. The calculations of these can be found in the settler section of appendix A6.XVI.

6.12.5 Practical Tips for Scale-up

In this case the volumetric flow rates are at the low side meaning that there will be no problem concerning the feed that it would leave residual jets or major turbulence at the inlets. When scaling up this could very well change. A solution to these problems could then be provided by a feed diffuser inside the settler placed a little in front of the inlet. It would consist of two plates or two rows of bars with the first row providing the high pressure drop and the second one breaking up the jets of the first row to introduce the feed uniformly across the active cross section of the settler. The energy in the jets will then be dissipated as turbulence. One must keep in mind the pressure drop, which has to be many times higher than the pressure drop down the settler to force distribution, and the peak velocity leaving the diffuser, this should be only 2 to 5 times the mean velocity down the settler. If use of a scale model yields unsatisfactory results, use of plates in the separator will always enhance performance of the settler. This is because of the larger settling area achieved. One must keep in mind that this is more expensive though then a simple vessel. This also concludes the discussion on the separation of the dispersion coming out of the second reactor.

6.12.6 Cost Estimation

Because of the simplicity of the settler the cost calculation is arbitrary. The total cost of the settler is fl. 7,000.- (see volume II).
6.12.7 Conclusions

With the density difference of the two phases in the dispersion $d_p$ being 90 kg/m$^3$, separation by settling is possible. The temperature chosen is $t=200^\circ$ C, this choice is made because of the place that the settler takes within the process scheme. The pressure at this temperature is put at 2 bars in order to make sure that none of the components in the mixture evaporate or decompose, this especially implies the MEG which at atmospheric pressure has an vaporization temperature of $190^\circ$. In order to meet all the criteria it is necessary to design a settler with an interface area of 3.5 times the minimum necessary settling area. This will not give constructive problems so that a plate separator, which is always more expensive, would be necessary. The level of the interface within the settler is crucial. This means that a level controller is necessary. The complete calculation as well as a list of the results of the settler design can be found in appendix A6.XVI.
6.13 The Distillation Column

6.13.1 Introduction

This separation column should separate the MEG from the Rrigids and DADPM. The mixture Rrigids DADPM will then enter a vessel in which the DADPM is propoxylated. The MEG coming from this separator (called crude MEG) will be used again in the extractor and the reactor. MEG is more volatile than DADPM and Rrigids and will go over the top of the column. MEG will be taken as the light key component and DADPM as the heavy key component.
6.13.2 Specifications and Physical Properties

The feed consists of 10600 kg/h MEG, 351 kg/h Rigid and 31.1 kg/h DADPM. The specification for the top product (crude MEG) is 20 ppm (mass) DADPM, so that it can be used quite well in the extractor and in the reactor. The specification for the bottom product is MEG : DADPM = 328.5 : 60.7 (mass). There is no real specification for the Rigid but it is assumed that the concentration of Rigid at the top shouldn’t exceed 20 ppm (mass). This won’t be a problem as the Rigid are less volatile than DADPM.

This leads to Table 6.4.

The main physical properties used in the required calculations are:

Saturation pressure:

MEG: \( \ln P_{\text{sat}} = 20.53 - 6022.2/(T - 28.25) \) (ChemCad database)

DADPM: \( \ln P_{\text{sat}} = 23.1 - 10526/T \) (ICI data)

Rigid: \( \ln P_{\text{sat}} = 139.25 - 21515/T \) - Riedel Equation [10], for derivation see appendix A6.XVII.

\( P_{\text{sat}} \) in mbar and \( T \) in Kelvin

Viscosity:

MEG: \( \log \eta = 1365/T - 6.392 \) (Chemcad database)

Bottom stream of the separation column: \( \ln \eta = 6.69e3/T - 19 \) (data from our experiments carried out with samples from ICI)

Viscosity \( \eta \) in Pa.s and \( T \) in Kelvin.

From these data a figure can be drawn showing \( \ln P_{\text{sat}} \) versus \( 1/T \). The relative volatility (\( \alpha_{\text{MD}} \)) of MEG-DADPM is \( P_{\text{sat}}^{\text{MEG}} / P_{\text{sat}}^{\text{DADPM}} \), so \( \ln \alpha_{\text{MD}} \) is \( \ln P_{\text{sat}}^{\text{MEG}} / \ln P_{\text{sat}}^{\text{DADPM}} \).

It’s obvious that the separation will be best at low temperatures!

6.13.3 Why a Flash Vessel won’t be Sufficient

The mixture is assumed to be an ideal solution and the gas to be an ideal gas. Although separation is best at low temperatures, from an energetic point of view it’s favourable to keep the temperature of the feed (coming from the settler) as high as possible, because heat will be required to evaporate MEG in the separation column.

The temperature of the feed will be approximately 190°C.
Calculations for an isothermal flash are carried out for the binary system MEG-DADPM as well as the tertiary system MEG-DADPM-Rigids, in a pressure range varying from 0.1 to 1.0 bar. The temperature in the vessel will then vary from 135°C to about 200°C. An adiabatic flash won’t be possible because the amount of energy needed to evaporate the (large amount of) MEG can’t be obtained from cooling down the mixture.

The isothermal flash calculations show that even the most favourable conditions won’t lead to the desired separation:

- mol fraction of DADPM in the top: \( y_{DADPM} = 86.557 \times 10^{-6} \) (= 275 ppm);
- total MEG flow over the top: \( 10.44 \times 10^3 \) kg/h MEG (recovery 98.5 %).

For the complete calculations see appendix A6.XVIII.

This result could be predicted quite easy with Raoult’s Law:

\[
\begin{align*}
    y_{MEG} \cdot P &= x_{MEG} \cdot P_{sat\; MEG} \\
    y_{DADPM} \cdot P &= x_{DADPM} \cdot P_{sat\; DADPM}
\end{align*}
\]

from which can be derived:

\[
\alpha_{MD} = \frac{y_{MEG}}{y_{DADPM}} \cdot \frac{x_{DADPM}}{x_{MEG}}
\]  

(6.36)

When the specifications are filled in this formula it follows that the required \( \alpha_{MD} \) should be about 9200. However \( \alpha_{MD} \) is about 450, as can be derived from figure 6.12.

It’s possible of course to connect a second flash to the bottom or to the top (after condensation of the top stream). But even with a second flash the desired separation won’t be achieved and the extra energy and capital costs for an extra flash vessel make this solution not attractive.

The conclusion is that a flash vessel isn’t sufficient and a distillation column has to be considered.
6.13.4 Distillation Calculations

These calculations can be divided in two parts i.e. determination of number of theoretical trays and reflux ratio and finally the column sizing.

6.13.4.1 Number of Theoretical Trays/Reflux Ratio

Different ways of calculating this number are considered: the McCabe-Thiele method, the Smoker Equations and a short-cut method on Chemcad. In order to be able to use the McCabe-Thiele method or the Smoker Equations the ternary system has to be reduced to a binary system. MEG is then taken as the light key component and DADPM as the heavy key component. However it's not possible to draw a McCabe Thiele diagram because of the extreme specification in the top product! (see Appendix A6.XIX.). And the Smoker Equations should only be applied when the relative volatility is no more than 2. In our case the relative volatility is approximately 450, so neither this method can be used. So only Chemcad remains. Only the short-cut method is used because it's not likely that the conditions in the column will vary that much through the column that a rigorous method (calculating from stage to stage) is required. But also this method has disadvantages. There are no physical properties available for the Rigid, so Chemcad estimates some properties from the molecular formula (group contribution method). It's nearly the same with the DADPM, because only the saturation pressure is known. So it could be that Chemcad's calculations are not that reliable. Because of this danger there are also calculations carried out for the binary system MEG-DADPM because from these two we have at least reliable values for the saturation pressure. However also a distillation calculation was carried out for the original tertiary system. If you are interested in these calculations, see appendix A6.XX. Here only the worst case (highest number of theoretical trays) is mentioned:

- minimum reflux: very low, about 1e-05;
- minimum number of trays: 1.88;
- number of theoretical trays: 3.67;
- calculated reflux ratio: 0.24.

From this very low minimum reflux it can be derived that the reflux ratio won't have much influence on the separation achievement of the column.

6.13.4.2 Column Sizing

Once the parameters mentioned above are known, the column can be sized. This means determination of number of real trays, packing length, diameter, etc., taking into account danger for flooding. Two columns are compared: the sieve trays and the structured packed column. A sensible possibility of these two is mentioned here, another option of a packed column can be found in appendix A6.XXI. The calculations behind these figures can be found in [11].
Although both these options will meet the specifications, there are of course differences.

The packed column requires a certain minimum reflux ratio in order to keep the packing wet. The sieve trays column doesn’t have an under limit for the reflux ratio, because the hold-up on the trays can be adjusted by changing the weir height. From a separation point of view the reflux might be lowered a bit. This would mean a reduction of the reboiler heat duty and as just mentioned this doesn’t give a lot of trouble with a sieve trays column, but it is a problem with the packed column.

An advantage of the packed column is that it’s less sensitive for dropping through i.e. liquid dropping straight through the column when the gas flow rate in the column becomes too low. This makes this column more flexible in operating.

On the other hand an advantage (of the sieve trays column) is that when the capacity has to be changed or the specification sharpened even more, there (still) is a possibility to make it a packed column (without having to change a lot) which can handle these new requirements.

However, practical experience with these different types of columns should also have a major influence on the choice to be made.
6.13.5 Cost Estimation

A cost estimation [11] was done for two columns mentioned in paragraph 3.2.

The total costs of a distillation column can be divided in two parts:
* costs for the shell;
* costs for the internals.

1 The sieve trays column:

   shell: HFl 145,250.-
   internals: HFl 16,000.-

   Total costs: HFl 161,250.-

2 The packed column (with Mellapak Y250):

   shell: HFl 106,100.-
   internals: HFl 24,000.-

   Total costs: HFl 130,100.-

So the packed column is a bit cheaper but not much (19 %). The cost calculations can be found in volume II.
6.13.6 Conclusions and Recommendations

In order to achieve the desired separation of the MEG from the DADPM and Rigid a distillation column is required. This column should have 3.7 theoretical trays. This leads to a sieve trays column with 10 stages and 1.48 m diameter or to a structured packed column with a diameter of 1.35 m and a packing length of about 1.70 m.

The choice between these options strongly depends on personal experiences with these types. However the packed column will be more flexible in operating while on the other hand the trays column will be easier to adjust when flow-rates or specifications have to be changed severly. The prices of these options will be nearly equal.


**Literature**


5. Perry's Handbook of Chemical Engineering

6. Amafilter B.V. Postbus 396, 1800 AS, Alkmaar, Holland
   J. van't Hart, Dhr. P. Mousen.


11. Z. Olujic, *Approximate design and costing of equipment used in absorption*, distillation, extraction and stripping processes, T.U. Delft.
7 WORK-UP SECTION

7.1 List of Symbols

\begin{itemize}
  \item \textbf{a} \hfill \text{interfacial area [m}^2\text{]} \\
  \item \textbf{A}_o \hfill \text{total cross-sectional area of bed [m}^2\text{]} \\
  \item \textbf{A}_b \hfill \text{bubbling area [m}^2\text{]} \\
  \item \textbf{A}_d \hfill \text{downcomer area [m}^2\text{]} \\
  \item \textbf{A}_h \hfill \text{hole area [m}^2\text{]} \\
  \item \textbf{A}_p \hfill \text{pulsation amplitude [m]} \\
  \item \textbf{A}_T \hfill \text{tower cross-sectional area [m}^2\text{]} \\
  \item \textbf{B} \hfill \text{permeability coefficient [m}^2\text{]} \\
  \item \textbf{c} \hfill \text{capacity of resin [meq/gram]} \\
  \item \textbf{c}_p \hfill \text{specific heat [J/kg.K]} \\
  \item \textbf{d} \hfill \text{diameter of particle [m]} \\
  \item \textbf{d}_h \hfill \text{hole diameter [m]} \\
  \item \textbf{d}_m \hfill \text{equivalent diameter of the pore channel [m]} \\
  \item \textbf{d}_m \hfill \text{maximum drop diameter [m]} \\
  \item \textbf{d}_m \hfill \text{mean drop diameter [m]} \\
  \item \textbf{d}_{\text{min}} \hfill \text{diameter of smallest drop [m]} \\
  \item \textbf{d}_{\text{sep}} \hfill \text{diameter of separator [m]} \\
  \item \textbf{d}_o \hfill \text{drop diameter without pulsation [m]} \\
  \item \textbf{d}_p \hfill \text{packing diameter [m]} \\
  \item \textbf{d}_t \hfill \text{diameter of tube [m]} \\
  \item \textbf{d}_{3,2} \hfill \text{Sauter mean drop diameter [m]} \\
  \item \textbf{D} \hfill \text{column diameter [m]} \\
  \item \textbf{e} \hfill \text{fractional voidage of bed [-]} \\
  \item \textbf{E} \hfill \text{extraction factor [-]} \\
  \item \textbf{E}_M \hfill \text{Murphree tray efficiency dispersed phase [-]} \\
  \item \textbf{E}_0 \hfill \text{Eötvös number [-]} \\
  \item \textbf{f} \hfill \text{pulsation frequency [1/s]} \\
  \item \textbf{F} \hfill \text{feed rate [kg/h]} \\
  \item \textbf{Fr} \hfill \text{Froude number [-]} \\
  \item \textbf{g} \hfill \text{gravity [m/s}^2\text{]} \\
  \item \textbf{h} \hfill \text{operational hold-up [-]} \\
  \item \textbf{h}_i \hfill \text{height of liquid level [m]} \\
  \item \textbf{h}_{\text{max}} \hfill \text{maximum hold-up [-]} \\
  \item \textbf{H} \hfill \text{height of compartment [m]} \\
  \item \textbf{HC} \hfill \text{heavy component} \\
  \item \textbf{H}_{\text{dr}} \hfill \text{height of drop rise zone [m]} \\
  \item \textbf{HDU} \hfill \text{height of diffusion unit [m]} \\
  \item \textbf{HETS} \hfill \text{height equivalent theoretical stage [m]} \\
  \item \textbf{HTU} \hfill \text{height of mass transfer unit [m]} \\
  \item \textbf{k} \hfill \text{mass transfer coefficient [m/s]} \\
  \item \textbf{K} \hfill \text{dimensionless constant [-]}
\end{itemize}
K  mass distribution coefficient [-]
K_i  K-value of component i [-]
K_o  overall mass transfer coefficient [m/s]
K_d  overall mass transfer coefficient in drop rise zone [m/s]
K'  dimensionless constant [-]
l  thickness of bed [m]
l_c  length of channel [m]
l_t  length of circular tube [m]
L  extraction length [m]
L_TOT  column length [m]
m  (molar/mass) distribution coefficient [-]
M  molecular mass [gram/mol]
M_G  mass flow rate of gas phase [kg/s]
M_L  mass flow rate of liquid phase [kg/s]
n  number of revolutions [1/s]
N  number of plates [-]
N_h  number of holes [-]
N_{th}  number of theoretical stages [-]
p  pitch [m]
p  pressure [bar] or [mm Hg]
P  Péclet number per unit height [1/m]
-ΔP  pressure drop across bed [N/m²]
Q  mass flow rate [kg/h]
Q  volumetric flow rate [m³/s]
R  rotor diameter [m]
R_d  drag force per unit area of particles [N/m²]
Re  Reynolds number [-]
Re_l  modified Reynolds number [-]
S  solvent rate [kg/h]
S  stator diameter [m]
S  specific surface area per unit volume of particle [m²/m³]
S_B  specific surface area per unit volume of bed [m²/m³]
S_p  surface area [m²/m³]
Sh  Sherwood number [-]
t  residence time [s]
t  temperature [°C]
T  temperature [K]
T_s  tray spacing [m]
u  average velocity based on cross-sectional area of
  vapour velocity [m/s]
U  velocity [m/s]
U_{CD}  velocity of continuous phase in the downcomer [m/s]
U_h  hole velocity [m/s]
U_o  terminal drop velocity [m/s]
U_s  slip velocity [m/s]
V  superficial velocity [m/s]
V_{bed}  volume of bed [m³]
V_L  liquid volume [m³]
V_o  characteristic velocity [m/s]
\( V_{\text{slip}} \)  
\( W_r \)  
\( \text{We} \)  
\( x \)  
\( y \)  

\textbf{Greek symbols}  
\( \alpha \) relative volatility [-]  
\( \delta \) diffusivity/diffusion coefficient \([\text{m}^2/\text{s}]\)  
\( \Delta \rho \) density difference \([\text{kg}/\text{m}^3]\)  
\( \varepsilon \) power input per mass unit \([\text{W/kg}]\)  
\( \eta \) viscosity \([\text{Pa.s}]\)  
\( \phi \) hold-up fraction [-]  
\( \mu \) viscosity of flexible \([\text{Pa.s}]\)  
\( \omega \) coalescence constant [-]  
\( \Omega \) fraction void space [-]  
\( \rho \) density \([\text{kg}/\text{m}^3]\)  
\( \rho_f \) density of flexible \([\text{kg}/\text{m}^3]\)  
\( \sigma \) interfacial tension \([\text{N/m}]\)  
\( \sigma_f \) surface tension feed \([\text{N/m}]\)  
\( \sigma_s \) surface tension solvent \([\text{N/m}]\)  

\textbf{Subscripts}  
\( \text{ax} \) axial  
\( \text{bubble} \) bubble point  
\( \text{bottom} \) bottom of column  
\( \text{c} \) continuous phase  
\( \text{d} \) dispersed phase  
\( \text{DADPM} \) di amine di phenyl methane  
\( \text{dew} \) dew point  
\( \text{e} \) effective  
\( \text{E} \) extract  
\( \text{f} \) flooding  
\( \text{F} \) feed  
\( \text{g,G} \) gas  
\( \text{i} \) component i  
\( \text{l, L} \) liquid  
\( \text{MEG} \) mono ethylene glycol  
\( \text{N} \) raffinate  
\( \text{sat} \) saturated liquid  
\( \text{S} \) solvent  
\( \text{t} \) total  
\( \text{top} \) top of column
7.2 Summary Work-up Section

The work-up section removes the excess of MEG and DADPM in the flexible stream to the amount of the required specifications. Therefore we use the processes extraction, distillation and ion-exchange.

The largest amount of DADPM is removed by the extraction process. The Rotary Disc Contactor, Pulsed Packed Column and Sieve Plate Column are chosen to be further elaborated at temperatures of 80°C and 100°C. After design, cost calculation and operating characteristics have been determined, we consider the Rotary Disc Contactor and an operating temperature of 80°C to be the best possible solutions for the extraction process.

MEG has to be separated from DADPM and Flexibles in a distillation column. Flexibles cannot be distilled, it is a heavy bottom product, so the binary system with MEG and DADPM is considered.

The relative volatilises of MEG and DADPM are calculated and a McCabe-Thiele diagram is drawn; it shows that one tray meets the required separation. Perhaps a flash vessel meets the requirement of less than 0.1 % MEG in the bottom product.

An isothermal flash is calculated at 188 °C, 190 °C, 192 °C, 198 °C, 200 °C and a feed pressure 1.1 bar. At higher temperatures a less deep vacuum (0.20 bar) is required to get less than 0.1 % MEG in the bottom product and a low heat duty (4.02 M Joule/h at 200 °C) is required.

An adiabatic flash is calculated at 190 °C, 195 °C, 200 °C and a feed pressure 1.1 bar and at 190 °C, 195 °C, 200 °C and a feed pressure 1.0 bar. Again, a less deep vacuum is required at higher temperatures to meet the requirement of less than 0.714 kg/h MEG in the bottom product.

At 0.20 bar in the top and the bottom the corresponding temperatures in the top and the bottom are 198.1 °C.

The diameter of the flash vessel is 0.60 m and the height is 2.02 m.

In the ion-exchanger the quantity of DADPM in Flexibles must be decreased to less than 20 ppm.

Two methods have been discussed: - The 'batch' process

- The 'continuous' process

Cation exchanger Amberlyst 15 is used to remove the DADPM from the Flexibles. The resin is reactivated with a HCl solution by the regeneration process. For the removal of DADPM from Flexibles with the help of the 'batch' process one storage (3 m³) and one column (V_{bed} = 0.011 m³) are used.

After the regeneration process, the resin must be dried before it can be used again for the adsorption process.

The 'continuous' process uses two columns parallel. This process is more favourable than the batch process because the total costs of the continuous process are lower than the total cost of the batch process.
7.3 Introduction Work-up Section

After the separation of the flexibles and the rigids in the settler, the work-up section leads to purification of the flexible stream, which contains MEG and DADPM. The excess of MEG and DADPM is to be removed in order to obtain a product (flexibles) that contains less than 20 p.p.m. DADPM. The DADPM removal is to be realized through the processes extraction, distillation and ion-exchange.

In this chapter we will try to make a justified selection of the equipment to use in order to reach the demanded specifications. After design and cost calculations have been made the equipment will successively be discussed.
7.4 The Extraction Process

7.4.1 Introduction Extraction

Liquid-liquid extraction or solvent extraction is a separation process which is based on the different distribution of the components to be separated between two liquid phases. It depends on the mass transfer of the component to be extracted from a first liquid phase into a second one.

As we can see in the Process Flow Diagram the liquid-liquid extraction process is used to remove the unwanted DADPM from the flexible-phase, which has a composition of 84% flexibles, 14% MEG and 1% DADPM (weight percentages), until we reach a DADPM mass concentration with a maximum of 0.05% (specification).

There is a large number of extraction equipment we can use for this liquid-liquid extraction. A summary of several equipments and their characteristics are given in appendix A.7.1.

The calculated number of theoretical stages required, the density difference between the two phases, and the availability of design calculation equations are several of the factors that lead to the choice of further elaboration of a few extraction columns.

First we will give a summary of the used extraction data and the number of theoretical stages will be calculated. After this the dimensions of the column will be calculated and a rough cost estimation is made. Finally the columns will be compared.

7.4.2 Extraction Data

For the extraction process [figure 7.1] several mass flow rates and compositions of streams are given or specified;

*) Feed composition: Flexibles with 15% MEG and 1% DADPM
*) Raffinate composition: Flexibles with 15% MEG and 500 p.p.m. DADPM
*) Our total-process-circumstances, work-up of 1 ton of polyurethane per hour, mixed in the proportion of 1 to 10 with MEG, gives a feed mass flow rate to the extractor of 850 [kg/h].
*) The solvent rate is an experimentally derived optimum. We need to take several things into consideration;
- a higher solvent rate leads to a column with larger diameter and smaller height, but also to higher heat exchange requirements (more cooling down and heating) because of larger flow rates
- a smaller solvent rate leads to a column with smaller diameter and larger height, with a minimum that is determined by constructive (im)possibilities. It also leads to less cooling down and heating of the streams
- several design demands as can be seen in the equipment design calculations need to be taken into consideration.

Therefore we choose a solvent flow rate of 841 [kg/h].
For the solving of the design equations we use the following in- and out-going streams and compositions:

<table>
<thead>
<tr>
<th></th>
<th>mass flow [kg/h]</th>
<th>FLEXIBLES</th>
<th>MEG</th>
<th>DADPM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[kg/h]</td>
<td>[kg/h]</td>
<td>[kg/h]</td>
</tr>
<tr>
<td>feed</td>
<td>850</td>
<td>714</td>
<td>127.5</td>
<td>8.5</td>
</tr>
<tr>
<td>solvent</td>
<td>841</td>
<td>-</td>
<td>840.983</td>
<td>0.017</td>
</tr>
<tr>
<td>raffinate</td>
<td>840.494</td>
<td>714</td>
<td>126.074</td>
<td>0.42</td>
</tr>
<tr>
<td>extract</td>
<td>850.506</td>
<td>-</td>
<td>842.409</td>
<td>8.09</td>
</tr>
</tbody>
</table>

For the solving of the design equations we use the following stream and component properties:

<table>
<thead>
<tr>
<th></th>
<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_f$ [kg/m$^3$]</td>
<td>994</td>
<td>979</td>
</tr>
<tr>
<td>$\rho_s$ [kg/m$^3$]</td>
<td>1070</td>
<td>1056</td>
</tr>
<tr>
<td>$\Delta \rho$ [kg/m$^3$]</td>
<td>76</td>
<td>85</td>
</tr>
<tr>
<td>$\eta_p$ [Pa.s]</td>
<td>96.6*10^{-3}</td>
<td>39.3*10^{-3}</td>
</tr>
<tr>
<td>$\eta_s$ [Pa.s]</td>
<td>3.1*10^{-3}</td>
<td>2.0*10^{-3}</td>
</tr>
<tr>
<td>$\sigma_p$ [N/m]</td>
<td>2.1*10^{-3}</td>
<td>1.9*10^{-3}</td>
</tr>
<tr>
<td>$\sigma_s$ [N/m]</td>
<td>43.2*10^{-3}</td>
<td>41.4*10^{-3}</td>
</tr>
<tr>
<td>$\sigma$ [N/m]</td>
<td>41.1*103</td>
<td>39.5*10^{-3}</td>
</tr>
<tr>
<td>$\delta_p$</td>
<td>2.2083*10^{-11}</td>
<td>5.7356*10^{-11}</td>
</tr>
<tr>
<td>$\delta_s$</td>
<td>2.779*10^{-10}</td>
<td>4.5508*10^{-10}</td>
</tr>
</tbody>
</table>

Appendix A.7.II contains more information, concerning these properties.
7.4.3 Calculation of Number of Theoretical Stages

Before we proceed with the design of several extraction equipments, the number of theoretical stages is determined. This number is influenced by solvent and feed rate and their composition, equilibrium data and the specifications of the raffinate.

To calculate the number of theoretical stages we can use the Kremser equation from Cusack [1];

\[
N_{th} = \frac{\log \left( \frac{x_f - \frac{y_s}{m}}{x_N - \frac{y_s}{m}} \cdot \frac{1}{1 - \frac{1}{E}} \right)}{\log E}
\]

where \(N_{th}\) is the number of theoretical stages, \(x_f\) is the concentration of solute in the feed and \(x_N\) the concentration of solute in the raffinate (with the feed and the raffinate on a solute-free basis), \(y_s\) is the concentration of solute in the solvent and \(E\) is the extraction factor.

The equation can also be solved graphically as shown in figures 7.2 and 7.3, which is called McCabe-Thiele diagrams.

At a reaction temperature of 80°C we find a number of theoretical stages between three and four in both cases. At a temperature of 100°C we find a value between 22 and 23. Calculations will be done with 4 and 23 stages at 80°C and 100°C respectively.

7.4.4 Equipment Design

As we can see in the diagram from Zuiderweg [2] (figure 7.3) the number of required theoretical stages, the density difference and the interfacial tension are parameters on which we can base our decision to reduce the extractor equipment to only a few equipments for further elaboration. So are the characteristics of several equipment as given in appendix A.7.1.

Furthermore we note that the design of extraction equipment and systems has been largely in the hands of equipment suppliers.

Taking all this in consideration the following equipment is chosen to be designed:
1. Rotary Disc Contactor (RDC)
2. Pulsed Packed Column (PPC)
3. Sieve Plate Column

7.4.4.1 Rotary Disc Contactor

The Rotary Disc Contactor (figure 7.5) is a mechanically agitated extraction column. Initially developed in the late 1940s and early 1950s to process lubricating oils, this column has found wide use in the petroleum and chemical industries.
The RDC consists of a series of rotors/discs mounted on a central shaft (which provides the extra energy for dispersion) located within a series of stator rings. The rotating discs fling the drops of the dispersed phase off centrifugally, onto the stator rings where they are broken and deflected. These stators limit axial mixing and define the mixing stages in the vessel. The vertical shaft is placed in such a way that the rotors find themselves exactly between two stators. The operation of the shaft can take place at the top, as well as at the bottom of the RDC. At the far end of the column there is a grid that reduces the turbulence caused by the rotating of the discs, in order to let the settling take place. The rotating discs cause a complex agitation pattern (figure 7.6). Because of combination of the horizontal and pulsating streams, there is a thyroidal stream in every compartment.

In design equations we generally use the ratios of column diameter (D), stator diameter (S), rotor diameter (R) and height of compartment (H) as they are given in figure 7.5.

Our equipment design concerns column diameter (D), stator diameter (S), rotor diameter (R), compartment height (H) and total column height, all influenced by the droplet size of the dispersed phase (adjustable by the rotation speed of the rotors) and the mass flow rate of feed and solvent. The calculated design procedure is given in detail in appendix A.7.III. The results are:

<table>
<thead>
<tr>
<th></th>
<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [m]</td>
<td>0.384</td>
<td>0.383</td>
</tr>
<tr>
<td>S [m]</td>
<td>0.269</td>
<td>0.268</td>
</tr>
<tr>
<td>R [m]</td>
<td>0.192</td>
<td>0.191</td>
</tr>
<tr>
<td>H [m]</td>
<td>0.077</td>
<td>0.077</td>
</tr>
<tr>
<td>L_{TOT} [m]</td>
<td>10.32</td>
<td>28.17</td>
</tr>
</tbody>
</table>

7.4.4.2 Pulsed Packed Column

The Pulsed Packed Column (PPC) (figure 7.7) has been developed by DSM and has been in production on industrial scale since 1970. This column is also mechanically agitated. A pulsed packed column consists of a vertical cylindrical vessel partly filled with packing rings. Two liquid phases, one of which is present in the form of drops, pass countercurrently through the column. In the top, or base, of the column, the dispersed phase coalesces at an interface layer. The two phases in the column are moved up and down by means of a pulsing device, connected to the column base. The pump-pulsator is the most used pulsing device (figure 7.8), as are the Raschig rings the most used packings. The required energy for this pulsation method is almost equal to that required by other mechanically agitated extraction equipment. The packing aids the formation of drops, which helps mass transfer and also lessens axial mixing. However it restricts the free area for flow of the fluids and thus hinders
throughput. Formation of a liquid film by the dispersed phase can be counterproductive since it may reduce the interfacial area.

The design equations used to determine height, diameter and other characteristic dimensions of the column are discussed in detail in appendix A.7.IV. To solve these equations the extraction data from paragraph 7.4.2 are used. The results of column diameter and total column height are:

<table>
<thead>
<tr>
<th></th>
<th>80°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>D [m]</td>
<td>1.17</td>
<td>1.18</td>
</tr>
<tr>
<td>L_{TOT} [m]</td>
<td>25.06</td>
<td>54.00</td>
</tr>
</tbody>
</table>

7.4.4.3 Sieve Plate Column

Sieve Plate Columns (figure 7.9) contain a series of perforated plates plus 'downcomers' or 'upcomers', depending on which phase is dispersed. The Sieve Plate extractor works on the principle of successive coalescence and regeneration of the dispersed phase, so it operates as a stagewise contactor. Each sieve plate provides a site for the dispersed phase to coalesce, and the holes in the plate regenerate the droplets. Therefore besides having a principal interface at either the top or bottom of the column, the sieve plate extractor also has a number of intermediate interfaces, one for each tray.

In order to determine the actual size of this apparatus the following strategy is followed:

1) -choose the perforation (or hole) diameter, generally 3<\text{d}_h<8\text{ mm};
   -choose a triangular pitch, generally 12<\text{p}<20\text{ mm}
   By choosing these variables the area's of the column, the downcomer and the perforated area are determined. It can be proven that in this case an optimal performance is reached at \text{d}_h=3.71\text{ mm en p}=12\text{ mm}.

2) -choose a tray spacing, generally 0.4 m.
   By choosing a tray spacing the number of plates and the height of the column are determined. The overall efficiency of a tray is a function of tray spacing. The bigger the tray spacing the greater the overall tray efficiency. Because the tray spacing has to have a reasonable value (regarding constructive aspects), is chosen for a tray spacing of 0.6 m.

The outcome of this procedure as well as the used equations are given in appendix A.7.V.
The results are:

<table>
<thead>
<tr>
<th></th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_h$ [mm]</td>
<td>3.71</td>
</tr>
<tr>
<td>$p$ [mm]</td>
<td>12</td>
</tr>
<tr>
<td>$A_h$ [m$^2$]</td>
<td>0.016</td>
</tr>
<tr>
<td>$A_s$ [m$^2$]</td>
<td>0.0646</td>
</tr>
<tr>
<td>$N_s$ [-]</td>
<td>84</td>
</tr>
<tr>
<td>$D$ [m]</td>
<td>0.42</td>
</tr>
<tr>
<td>$T_s$ [m]</td>
<td>0.6</td>
</tr>
<tr>
<td>$N$ [-]</td>
<td>23</td>
</tr>
<tr>
<td>$L_{TOT}$ [m]</td>
<td>19.2</td>
</tr>
</tbody>
</table>

7.4.5 Rough Cost Calculation

For this calculation we use the 'WEBCI/WUBO PRIJZENBOEKJE'[10], the Olujic [6] and a cost estimation made by: Verenigde Bedrijven Tankfabriek-Kooiman B.V.

We find:

1. ROTARY DISC CONTACTOR

(*) 1 column:
- outer diameter 406 [mm] (standard 16'' pipe)
- cylindric length of approx 10000 [mm]
- wall thickness 9.5 [mm]
- 2 brackets, 4 nozzles 4'' 150 lbs.
- 154 stator rings inside

Dfl. 50,000.-

(*) 1 rotor with 153 discs

Dfl. 2,000.-

(*) 1 electromotor (1500 [W]) and transmission

Dfl. 5,000.-

This leads to a total of

Dfl. 57,000.-

Note: The stator rings are not fixed to the column wall, because of the small diameter, but are designed to be held in place by a construction of equally distanced bars. This construction is made in two parts, so two column separations by standard s.o. flanges are necessary.
2. PULSED PACKED COLUMN

(*) 1 column;
   outer diameter 1190 [mm]
   cylindrical length of approx 25 [m]
   wall thickness 10 [mm]
   1 conical skirt, 4 nozzles 8” 150 lbs (2 inlet, 2 outlet),
   3 nozzles 2” 150 lbs (2 interface level control nozzles,
   1 vent nozzle)
   1 connection for rotary valve pulsator (Ø 400 [mm])
   2 manholes Ø 20” 150 lbs. with davit.  
   Dfl. 125,000.-

(*) Random packings (19 [mm] Raschig rings, Dfl. 13,000.- per m³)
   Dfl. 240,000.-

(*) Pulsating device
   Dfl. 5,000.-

This leads to a total of
   DFL. 370,000.-

3. SIEVE PLATE COLUMN

   outer diameter 457 [mm] (standard pipe 18”)
   cylindrical length of approx 19 [m]
   wall thickness 9.5 [mm]
   1 skirt of approx 1.5 [m]
   4 nozzles 4” 150 lbs.
   23 trays plus downcomers  
   Dfl. 80,000.-

Note: The trays with downcomers are not fixed to the column wall
because of the small diameter, but are designed to be held in place
by a construction of equally distanced bars. This construction is
made in three parts, so three column separations by standard s.o.
flanges are necessary.

7.4.6 Discussion

Because of the relatively small diameter compared to the height of the sieve plate
extractor and the large number of plates, maintenance of the column will be difficult.
The cleaning of the column when plugging occurs (caused by contamination), occurs
will be quite difficult. Sieve plate columns are very susceptible to solids plugging. They
also have a narrow range in regard to throughput.
Pulsed packed columns have a higher efficiency than sieve plate extractors because of
the oscillating pulse to the contents of the column. They are insensitive to silica
contamination in the feed stream. These columns contain quite expensive internals.
Rotary disc contactors maintain dispersion over a wide range of operating conditions at reasonable costs, there are many stages possible and they are relatively easy to scale up. They are relatively insensitive to undissolved solids and formation of stable emulsions because of flexible operation possibility.

Furthermore the rotary disc contactor is the cheapest option and also regarding safety (smallest volume, containing toxic liquids), operation and maintenance the most likely option to choose.
7.5 Distillation Process

7.5.1 Introduction

The feed to the separator is 714 kg/h Flexibles, 126 kg/h MEG and 0.42 kg/h DADPM. MEG has to be separated from Flexibles and DADPM in a distillation column or a flash vessel under such conditions that there is less than 0.1 % MEG in the bottom product, which is equivalent to 0.714 kg/h MEG in the bottom product.

7.5.2 Theory

At this separation there is a ternary system with three components: MEG, DADPM and Flexibles. Boiling point of MEG is 198 °C, molecular weight is 62.068. Boiling point of DADPM is 400 °C, molecular weight is 198.30. Flexibles is a polymer, that cannot be distillated, because it analyses before its boiling temperature. The molecular weight is 5000: Flexibles is a heavy bottom product from distillation column.

Because of the heavy Flexibles, which cannot be distillated, there is calculated at a binary system with two components: MEG is the light component and DADPM the heavy one.

First the saturated vapour pressure of MEG is calculated with the following Antoine equation:

\[ \log p_{\text{sat}}(\text{MEG}) = 6.9500 - \frac{1342.051}{132.139 + t} \]  

(7.1)

with: \( p_{\text{sat}}(\text{MEG}) = \) saturated vapour pressure of MEG (mm Hg), 
\( t = \) temperature (°C).

Then the saturated vapour pressure of DADPM is calculated with the following formula (7.2) and second with formula (7.3):

\[ \ln p_{\text{sat}}(\text{DADPM}) = 27.737 - \frac{10526}{T} \]  

(7,2)

with: \( p_{\text{sat}}(\text{DADPM}) = \) saturated vapour pressure of DADPM (Pa), 
\( T = \) temperature (K).

\[ \ln p_{\text{sat}}(\text{DADPM}) = 24.914 - \frac{9009.7}{T} \]  

(7,3)

with: \( p_{\text{sat}}(\text{DADPM}) = \) saturated vapour pressure of DADPM (Pa), 
\( T = \) temperature (K).

Formula (7.2) and (7.3) from experimental pressure data of I.C.I.
Bubble point and dew point calculations are done from formulas (7.4) and (7.5):

\[ P_{\text{BUBBLE}} = x_{\text{MEG}} \cdot p_{\text{sat}}(\text{MEG}) + x_{\text{DADPM}} \cdot p_{\text{sat}}(\text{DADPM}) \]  

(7.4)

with:
- \( P_{\text{BUBBLE}} \) = bubble point pressure,
- \( x_{\text{MEG}} \) = fraction MEG in liquid phase,
- \( x_{\text{DADPM}} \) = fraction DADPM in liquid phase.

\[ P_{\text{DEW}} = \frac{1}{\frac{y_{\text{MEG}}}{p_{\text{sat}}(\text{MEG})} + \frac{y_{\text{DADPM}}}{p_{\text{sat}}(\text{DADPM})}} \]  

(7.5)

with:
- \( P_{\text{DEW}} \) = dew point pressure,
- \( y_{\text{MEG}} \) = fraction MEG in liquid phase,
- \( y_{\text{DADPM}} \) = fraction in liquid phase.

For more information about the separation there is made a McCabe-Thiele diagram. The equilibrium K-values of MEG and DADPM have to be calculated with formula (7.6):

\[ K_i = \frac{p_{\text{sat}(i)}}{p} \]  

(7.6)

with:
- \( K_i \) = K-value of component i,
- \( p_{\text{sat}(i)} \) = saturated vapour pressure of component i,
- \( p \) = total (system) pressure.

Then the relative volatily \( \alpha \) is calculated with formula (7.7):

\[ \alpha = \frac{K_{\text{LC}}}{K_{\text{HC}}} \]  

(7.7)

with:
- \( \alpha \) = relative volatily,
- \( \text{LC} \) = light component,
- \( \text{HC} \) = heavy component.

Relative volatily is calculated at the top of the distillation column (where the temperature is 198 °C, boiling point of MEG) and at the bottom (where the temperature is 400 °C, boiling point of DADPM).
For drawing a McCabe-Thiele diagram an average relative volatility is calculated with the following formula:

\[
\alpha = \sqrt{\alpha_{Top} \cdot \alpha_{Bottom}}
\]  

(7,8)

with: \( \alpha \) = average relative volatility,
\( \alpha_{Top} \) = relative volatility at the top,
\( \alpha_{Bottom} \) = relative volatility at the bottom.

Using formula (7,9) a McCabe-Thiele diagram can be drawn.

\[
y = \frac{\alpha \cdot x}{1 + x \cdot (\alpha - 1)}
\]  

(7,9)

with: \( \alpha \) = average relative volatility,
\( x \) = component in liquid phase,
\( y \) = component in vapour phase.

The size of the separator is calculated.

For vertical separating vessels, the maximum design vapour velocity is defined empirically as:

\[
u_{sep} = 0.035 \cdot \frac{\rho_v}{\rho_L}
\]  

(7,10)

with: \( u_{sep} \) = vapour velocity (m/s),
\( \rho_v \) = density of gas phase (kg/m³),
\( \rho_L \) = density of liquid phase (kg/m³).

In formula 7,10: \( u_{sep} \) is the value which is used without any correction for diameter calculation, using formula (7,11):

\[
d_{sep} = 1.13 \cdot \frac{M_G}{\rho_G \cdot u_{sep}}
\]  

(7,11)

with: \( M_G \) = mass flow rate of gas phase (kg/s),
\( d_{sep} \) = diameter of the flash vessel.

A disengagement height equal to the vessel diameter should be provided above the liquid level.
Poly Urethane Recycling

The liquid level depends on the hold-up time required for smooth operation and control, typically 10 minutes is allowed. The height of the liquid (level) is given by:

\[ h_L = \frac{V_L}{f} = \frac{4 \cdot V_L}{\pi \cdot (d_{sep})^2} \]  \hspace{1cm} (7,12)

with: \( h_L \) = height of the liquid level (m),
\( V_L \) = volume of the liquid (m³).

In formula (7,12) is \( V_L \) the volume of liquid, which follows from mass flow rate and given residence time:

\[ V_L = \frac{M_L}{P_L} \cdot t = \frac{M_L}{P_L} \cdot (600) \]  \hspace{1cm} (7,13)

with: \( M_L \) = mass flow rate of liquid phase (kg/s),
\( t \) = residence time (s).

The mixture (feed) inlet should be at least 0.3 m above the maximum liquid level (0.5 m is a good choice).

Also, the installation of mesh pad requires extra height in the gas disengagement space. Therefore, a height above liquid is usually set to 1.5 diameter of the vessel, and as a minimum value 1 m is recommended.

Separator height or total length should be within the range:

\[ 3 \leq \frac{h_{sep}}{d_{sep}} \leq 5 \]  \hspace{1cm} (7,14)

with: \( h_{sep} \) = height of the separating vessel,
\( d_{sep} \) = diameter of the separating vessel.
7.5.3 Results

With formulas (7.1), (7.2) and (7.3) the saturated vapour pressures of MEG and DADPM $p_{\text{sat}}(\text{MEG})$ and $p_{\text{sat}}(\text{DADPM})$ are calculated. Results are shown in table 1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$p_{\text{sat}}(\text{MEG})$ (Pa)</th>
<th>$p_{\text{sat}}(\text{DADPM})$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>198</td>
<td>102286.7</td>
<td>218.94</td>
</tr>
<tr>
<td>200</td>
<td>108217.5</td>
<td>240.64</td>
</tr>
<tr>
<td>220</td>
<td>183564.3</td>
<td>593.53</td>
</tr>
<tr>
<td>240</td>
<td>294179.0</td>
<td>1364.4</td>
</tr>
<tr>
<td>260</td>
<td>449306.0</td>
<td>2946.6</td>
</tr>
<tr>
<td>280</td>
<td>658599.2</td>
<td>6018.8</td>
</tr>
<tr>
<td>300</td>
<td>931810.5</td>
<td>11696</td>
</tr>
<tr>
<td>320</td>
<td>1278502</td>
<td>21733</td>
</tr>
<tr>
<td>340</td>
<td>1707798</td>
<td>38782</td>
</tr>
<tr>
<td>360</td>
<td>2228191</td>
<td>66719</td>
</tr>
<tr>
<td>380</td>
<td>2847383</td>
<td>111030</td>
</tr>
<tr>
<td>400</td>
<td>3572190</td>
<td>179258</td>
</tr>
<tr>
<td>218.94</td>
<td>593.53</td>
<td>1364.4</td>
</tr>
<tr>
<td>294179.0</td>
<td>2946.6</td>
<td>11696</td>
</tr>
<tr>
<td>658599.2</td>
<td>6018.8</td>
<td>21733</td>
</tr>
<tr>
<td>931810.5</td>
<td>11696</td>
<td>38782</td>
</tr>
<tr>
<td>1278502</td>
<td>21733</td>
<td>66719</td>
</tr>
<tr>
<td>1707798</td>
<td>38782</td>
<td>111030</td>
</tr>
<tr>
<td>2228191</td>
<td>66719</td>
<td>179258</td>
</tr>
</tbody>
</table>

Results from table 1 are shown in figure 7.10.

From formulas (7.1), (7.2), (7.4) and (7.5) DEW-points and BUBBLE-points are calculated:

At temperature = 200 °C: $p_{\text{Dew}}$ = 0.608 bar and $p_{\text{Bubble}}$ = 1.08 bar.
At temperature = 220 °C: $p_{\text{Dew}}$ = 1.19 bar and $p_{\text{Bubble}}$ = 1.83 bar.
At temperature = 300 °C: $p_{\text{Dew}}$ = 8.20 bar and $p_{\text{Bubble}}$ = 9.30 bar.

From formulas (7.1), (7.3), (7.4) and (7.5) second DEW-point and BUBBLE-point calculations are done:

At temperature = 200 °C: $p_{\text{Dew}}$ = 0.706 bar and $p_{\text{Bubble}}$ = 1.08 bar.
At temperature = 220 °C: $p_{\text{Dew}}$ = 1.30 bar and $p_{\text{Bubble}}$ = 1.83 bar.
At temperature = 260 °C: $p_{\text{Dew}}$ = 3.57 bar and $p_{\text{Bubble}}$ = 4.48 bar.

So the best temperature to separate MEG from DADPM and Flexibles is about 200 °C.
Poly Urethane Recycling

Work Up

For McCabe-Thiele diagram relative volatility is calculated from formulas (7,6), (7,7) and (7,8): \( \alpha_{\text{top}} = 449.6 \) and \( \alpha_{\text{bottom}} = 19.92 \).

Average relative volatility: \( \alpha_1 = 94.64 \).

And second calculation:

\( \alpha_{\text{top}} = 314.2 \) and \( \alpha_{\text{bottom}} = 35.23 \).

Average relative volatility: \( \alpha_2 = 105.2 \).

Relative volatility is higher at lower temperatures, then better separation.
At higher temperature probably more DADPM in the top product.

With formula (7,9) a McCabe-Thiele diagram can be drawn.
McCabe-Thiele 1 and 2 (from \( \alpha_1 \) and \( \alpha_2 \)) are shown in figure 7.11.
The McCabe-Thiele diagram shows, that one tray is needed. Perhaps gives a flash vessel enough separation.
Maximum quantity MEG allowed in the bottom product is 0.714 kg/h.

With an adiabatic flash: partial evaporation is produced by sudden reduction of stream pressure. No heat is fed to the flash vessel.
In the case of fixed temperature and if there is heat fed to the flash, we speak of an isothermal flash.

First an isothermal flash is calculated with Chem Cad: feed pressure 1.1 bar.
Feed temperature 188 °C, vapour fraction 0. Results are shown in table 2.
Feed temperature 190 °C, vapour fraction 0.864. Results in table 3.
Feed temperature 192 °C, vapour fraction 0.872. Results in table 4.
Feed temperature 198 °C, vapour fraction 0.889. Results in table 5.
Feed temperature 200 °C, vapour fraction 0.893. Results in table 6.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>2.72</td>
<td>0.0239</td>
</tr>
<tr>
<td>0.45</td>
<td>2.36</td>
<td>0.0273</td>
</tr>
<tr>
<td>0.40</td>
<td>2.04</td>
<td>0.0316</td>
</tr>
<tr>
<td>0.35</td>
<td>1.73</td>
<td>0.0368</td>
</tr>
<tr>
<td>0.30</td>
<td>1.44</td>
<td>0.0436</td>
</tr>
<tr>
<td>0.25</td>
<td>1.16</td>
<td>0.0528</td>
</tr>
<tr>
<td>0.20</td>
<td>0.905</td>
<td>0.0657</td>
</tr>
<tr>
<td>0.15</td>
<td>0.660</td>
<td>0.0853</td>
</tr>
<tr>
<td>0.10</td>
<td>0.428</td>
<td>0.119</td>
</tr>
<tr>
<td>0.05</td>
<td>0.208</td>
<td>0.188</td>
</tr>
</tbody>
</table>

At 0.15 bar in top and bottom: the heat duty is 112.8 M Joule/h.

7.19
TABLE 3: Isothermal flash at 190 °C, feed pressure 1.1 bar, vapour fraction 0.864. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.10 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>2.53</td>
<td>0.0267</td>
</tr>
<tr>
<td>0.45</td>
<td>2.21</td>
<td>0.0304</td>
</tr>
<tr>
<td>0.40</td>
<td>1.91</td>
<td>0.0350</td>
</tr>
<tr>
<td>0.35</td>
<td>1.62</td>
<td>0.0407</td>
</tr>
<tr>
<td>0.30</td>
<td>1.35</td>
<td>0.0480</td>
</tr>
<tr>
<td>0.25</td>
<td>1.10</td>
<td>0.0578</td>
</tr>
<tr>
<td>0.20</td>
<td>0.854</td>
<td>0.0715</td>
</tr>
<tr>
<td>0.15</td>
<td>0.624</td>
<td>0.0923</td>
</tr>
<tr>
<td>0.10</td>
<td>0.405</td>
<td>0.127</td>
</tr>
</tbody>
</table>

At 0.15 bar in top and bottom: the heat duty is 7.06 M Joule/h.

TABLE 4: Isothermal flash at 192 °C, feed pressure 1.1 bar, vapour fraction 0.872. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.05 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>2.37</td>
<td>0.0297</td>
</tr>
<tr>
<td>0.45</td>
<td>2.07</td>
<td>0.0337</td>
</tr>
<tr>
<td>0.40</td>
<td>1.79</td>
<td>0.0386</td>
</tr>
<tr>
<td>0.35</td>
<td>1.52</td>
<td>0.0447</td>
</tr>
<tr>
<td>0.30</td>
<td>1.27</td>
<td>0.0526</td>
</tr>
<tr>
<td>0.25</td>
<td>1.03</td>
<td>0.0631</td>
</tr>
<tr>
<td>0.20</td>
<td>0.807</td>
<td>0.0777</td>
</tr>
<tr>
<td>0.15</td>
<td>0.590</td>
<td>0.0996</td>
</tr>
<tr>
<td>0.10</td>
<td>0.384</td>
<td>0.136</td>
</tr>
<tr>
<td>0.05</td>
<td>0.187</td>
<td>0.208</td>
</tr>
</tbody>
</table>

At 0.15 bar in top and bottom: the heat duty is 6.22 M Joule/h.
TABLE 5: Isothermal flash at 198 °C, feed pressure 1.1 bar, vapour fraction 0.889. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.05 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.95</td>
<td>0.0401</td>
</tr>
<tr>
<td>0.45</td>
<td>1.72</td>
<td>0.0451</td>
</tr>
<tr>
<td>0.40</td>
<td>1.49</td>
<td>0.0512</td>
</tr>
<tr>
<td>0.35</td>
<td>1.28</td>
<td>0.0587</td>
</tr>
<tr>
<td>0.30</td>
<td>1.07</td>
<td>0.0682</td>
</tr>
<tr>
<td>0.25</td>
<td>0.873</td>
<td>0.0808</td>
</tr>
<tr>
<td>0.20</td>
<td>0.684</td>
<td>0.0980</td>
</tr>
<tr>
<td>0.15</td>
<td>0.503</td>
<td>0.123</td>
</tr>
<tr>
<td>0.10</td>
<td>0.328</td>
<td>0.163</td>
</tr>
<tr>
<td>0.05</td>
<td>0.160</td>
<td>0.238</td>
</tr>
</tbody>
</table>

At 0.20 bar in top and bottom: the heat duty is 4.39 M Joule/h.

TABLE 6: Isothermal flash at 200 °C, feed pressure 1.1 bar, vapour fraction 0.893. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.05 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.84</td>
<td>0.0440</td>
</tr>
<tr>
<td>0.45</td>
<td>1.62</td>
<td>0.0494</td>
</tr>
<tr>
<td>0.40</td>
<td>1.41</td>
<td>0.0559</td>
</tr>
<tr>
<td>0.35</td>
<td>1.21</td>
<td>0.0639</td>
</tr>
<tr>
<td>0.30</td>
<td>1.01</td>
<td>0.0740</td>
</tr>
<tr>
<td>0.25</td>
<td>0.827</td>
<td>0.0873</td>
</tr>
<tr>
<td>0.20</td>
<td>0.649</td>
<td>0.105</td>
</tr>
<tr>
<td>0.15</td>
<td>0.477</td>
<td>0.132</td>
</tr>
<tr>
<td>0.10</td>
<td>0.312</td>
<td>0.173</td>
</tr>
<tr>
<td>0.05</td>
<td>0.153</td>
<td>0.247</td>
</tr>
</tbody>
</table>

At 0.20 bar in top and bottom: the heat duty is 4.02 M Joule/h.

Results from the tables 2 up to 6 are shown in figure 7.12. Looking at the isothermal flash at 200 °C: to meet the requirement of less than 0.714 kg/h MEG in the bottom product, a few heat (4.02 M Joule/h) is required; so it may be possible to use an adiabatic flash.
An adiabatic flash is calculated with Chem Cad at feed temperature 190 °C, feed pressure 1.1 bar. Results are shown in table 7.

Feed temperature 195 °C, feed pressure 1.1 bar. Results in table 8.
Feed temperature 200 °C, feed pressure 1.1 bar. Results in table 9.
Feed temperature 190 °C, feed pressure 1.0 bar. Results in table 10.
Feed temperature 195 °C, feed pressure 1.0 bar. Results in table 11.
Feed temperature 200 °C, feed pressure 1.0 bar. Results in table 12.

**TABLE 7:** Adiabatic flash at feed temperature 190 °C, feed pressure 1.1 bar, vapour fraction 0.864. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.10 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>2.82</td>
<td>0.0225</td>
</tr>
<tr>
<td>0.40</td>
<td>2.13</td>
<td>0.0293</td>
</tr>
<tr>
<td>0.30</td>
<td>1.52</td>
<td>0.0402</td>
</tr>
<tr>
<td>0.20</td>
<td>0.959</td>
<td>0.0602</td>
</tr>
<tr>
<td>0.10</td>
<td>0.456</td>
<td>0.109</td>
</tr>
</tbody>
</table>

At 0.10 bar in top and bottom the corresponding temperature is 185.8 °C.

**TABLE 8:** Adiabatic flash at feed temperature 195 °C, feed pressure 1.1 bar, vapour fraction 0.882. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.10 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>2.30</td>
<td>0.0310</td>
</tr>
<tr>
<td>0.40</td>
<td>1.76</td>
<td>0.0397</td>
</tr>
<tr>
<td>0.30</td>
<td>1.26</td>
<td>0.0534</td>
</tr>
<tr>
<td>0.20</td>
<td>0.805</td>
<td>0.0780</td>
</tr>
<tr>
<td>0.10</td>
<td>0.386</td>
<td>0.135</td>
</tr>
</tbody>
</table>

At 0.10 bar in top and bottom the corresponding temperature is 191.9 °C.
TABLE 9: Adiabatic flash at feed temperature 200 °C, feed pressure 1.1 bar, vapour fraction 0.893. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.10 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.93</td>
<td>0.0407</td>
</tr>
<tr>
<td>0.40</td>
<td>1.49</td>
<td>0.0514</td>
</tr>
<tr>
<td>0.30</td>
<td>1.07</td>
<td>0.0680</td>
</tr>
<tr>
<td>0.20</td>
<td>0.690</td>
<td>0.0970</td>
</tr>
<tr>
<td>0.10</td>
<td>0.332</td>
<td>0.161</td>
</tr>
</tbody>
</table>

At 0.20 bar in top and bottom the corresponding temperature is 197.7 °C.

TABLE 10: Adiabatic flash at feed temperature 190 °C, feed pressure 1.0 bar, vapour fraction 0.878. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.10 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>2.74</td>
<td>0.0236</td>
</tr>
<tr>
<td>0.40</td>
<td>2.08</td>
<td>0.0306</td>
</tr>
<tr>
<td>0.30</td>
<td>1.48</td>
<td>0.0418</td>
</tr>
<tr>
<td>0.20</td>
<td>0.936</td>
<td>0.0625</td>
</tr>
<tr>
<td>0.10</td>
<td>0.445</td>
<td>0.113</td>
</tr>
</tbody>
</table>

At 0.10 bar in top and bottom the corresponding temperature is 186.6 °C.

TABLE 11: Adiabatic flash at feed temperature 195 °C, feed pressure 1.0 bar, vapour fraction 0.890. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.10 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>2.27</td>
<td>0.0318</td>
</tr>
<tr>
<td>0.40</td>
<td>1.73</td>
<td>0.0407</td>
</tr>
<tr>
<td>0.30</td>
<td>1.24</td>
<td>0.0546</td>
</tr>
<tr>
<td>0.20</td>
<td>0.794</td>
<td>0.0796</td>
</tr>
<tr>
<td>0.10</td>
<td>0.380</td>
<td>0.138</td>
</tr>
</tbody>
</table>

At 0.10 bar in top and bottom the corresponding temperature is 192.4 °C.
TABLE 12: Adiabatic flash at feed temperature 200 °C, feed pressure 1.0 bar, vapour fraction 0.899. Quantity MEG in the bottom product, quantity DADPM in the top product at 0.50 bar up to 0.10 bar.

<table>
<thead>
<tr>
<th>Pressure in top and bottom (bar)</th>
<th>MEG in bottom product (kg/h)</th>
<th>DADPM in top product (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.91</td>
<td>0.0414</td>
</tr>
<tr>
<td>0.40</td>
<td>1.47</td>
<td>0.0522</td>
</tr>
<tr>
<td>0.30</td>
<td>1.06</td>
<td>0.0690</td>
</tr>
<tr>
<td>0.20</td>
<td>0.683</td>
<td>0.0983</td>
</tr>
<tr>
<td>0.15</td>
<td>0.503</td>
<td>0.123</td>
</tr>
<tr>
<td>0.10</td>
<td>0.329</td>
<td>0.163</td>
</tr>
</tbody>
</table>

At 0.20 bar in top and bottom the corresponding temperature is 198.1 °C.

Results from the tables 7 up to 12 are shown in figure 7.13.

FLASH VESSEL SIZING.

density of the gas phase = 0.237 kg/m³.
density of the liquid phase = 921 kg/m³.
With formula (7,10) vapour velocity is calculated: \( u_{\text{sep}} = 2.18 \text{ m/s} \).
Mass flow rate of the gas phase: \( M_g = 0.0337 \text{ kg/s} \).
With formula (7,11) the diameter is calculated: \( d_{\text{sep}} = 0.289 \text{ m} \).
This is too small!
We calculate further with: \( d_{\text{sep}} = 0.60 \text{ m} \).
Mass flow rate of the liquid phase: \( M_L = 719 \text{ kg/h} =719/3600 \text{ kg/s} \).
Residence time = \( t = 20 \text{ minutes} = 1200 \text{ s} \).
With formula (7,13):
Volume of the liquid = \( V_L = 0.260 \text{ m}^3 \).
With formula (7,12):
Height of the liquid = \( h_L = 0.920 \text{ m} \).
Height of the separator = \( h_{\text{sep}} \):
\[
\begin{align*}
    h_{\text{sep}} &= h_L + 1.5 \times d_{\text{sep}} + (\text{extra height for the demister}) = \\
    &= 0.920 \text{ m} + 1.5 \times 0.60 \text{ m} + 0.20 \text{ m} = 2.02 \text{ m}.
\end{align*}
\]
So the diameter of the flash vessel is 0.60 m and the height is 2.02 m.

7.5.4 Discussion and Conclusion

Isothermal flash.
At 188 °C, vapour fraction 0: the heat duty is high, because the whole heat of vaporization of MEG has to be fed to the flash vessel.
At higher temperatures a fewer deep vacuum (0.20 bar) is required to get less than 0.1 % MEG in the bottom product and a low heat duty is required (4.02 M Joule/h at 200 °C).
At higher temperatures and at deeper vacuum there is more DADPM in the top product. We do not like much DADPM in the system, because DADPM is very poisonous. Because of the low heat duty an adiabatic flash is calculated.

Adiabatic flash. An adiabatic flash has the advantage, that the flash vessel is not heated. There is no heat duty. Here is also required a fewer deep vacuum (0.20 bar) at higher temperature (200°C) to meet the requirement of less than 0.714 [kg/h] MEG in the bottom product. At 0.20 bar in top and bottom the corresponding temperature in top and bottom is 198.1 [°C] (At an adiabatic flash: at higher temperatures and deeper vacuum more DADPM in the top product too).

Conclusion: Under these circumstances an adiabatic flash at feed temperature 200°C and feed pressure 1.0 bar is the best separator, because it is most easy to handle; no heat duty, less deep vacuum is required (0.20 bar).
7.6 The Ion-exchange Process

7.6.1 Introduction Ion-exchange

The liquid stream from the flash consists of Flexibles, MEG and DADPM. The DADPM in this liquid must be removed from Flexible and MEG with the help of the ion exchanger. There are two methods for the removal of DADPM from Flexible:
- The 'batch' process, consists of packed column and storage.
- The 'continuous' process, consists of two parallel columns.
These methods will be discussed and compared, to decide which method is to be preferred.

7.6.2 Theory

7.6.2.1 Principle of Ion-exchange

Principal of Ion-exchangers;
Ion exchangers are solid and suitably insolubilized high molecular weight polyelectrolytes which can exchange their mobile ions for ions of equal charge from the surrounding medium. The resulting ion exchange is reversible and stoichiometric with the displacement of one ionic species by another on the exchanger. Viewed in a different light, ion exchangers can be considered high molecular weight acids or bases with a high molecular weight cation, which can exchange their hydrogen or hydroxyl ions and thus are converted into high molecular weight salts.

A cation exchanger is said to be in the acid form (or alternatively the H form) when the exchangeable ion is the hydrogen ion, and in the salt form (or the A form) when the exchangeable cation is the cation A⁺. Similarly, an anion exchanger may be either in the base (or OH) form, or in salt (or B) form for the anion B⁻. [13].

Two broad classes of functional groups are recognized for both cation and anion exchanger, depending upon the degree of dissociation of the acid or base involved:

<table>
<thead>
<tr>
<th>Strong</th>
<th>Cation exchangers</th>
<th>Anion exchangers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphonic acid</td>
<td>-SO₂H</td>
<td>Quartenary grouping</td>
</tr>
<tr>
<td>Weak</td>
<td>Carboxylic acid</td>
<td>Tertiary grouping</td>
</tr>
<tr>
<td>-CO₂H</td>
<td>Phenolic</td>
<td></td>
</tr>
<tr>
<td>-OH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.26
The example, a cation exchanger with fixed sulphonic acid groups on a polymeric matrix \( R \) in the sodium form, which is used for the important application of water softening, i.e. the exchange against calcium ions according to the equation:

\[
2 \text{RSO}_3^+\text{Na}^+ + \text{Ca}^{2+} \rightarrow (\text{RSO}_3^-)_2\text{Ca}^{2+} + 2 \text{Na}^+
\]

\[
2 \text{RA}^+ + \text{C}^{2+} \rightarrow \text{R}_2\text{C}^{2+} + 2 \text{A}^+
\]

And by the apparent exchange constant relationship:

\[
K_c = \frac{[\text{R}_2\text{C}^{2+}][\text{A}^+]^2}{[\text{RA}^+]^2[\text{C}^{2+}]} (7,15)
\]

with \([\text{RA}^+]\) and \([\text{R}_2\text{C}^{2+}]\) the concentrations of the ions in the resin and \([\text{A}^+]\) and \([\text{C}^{2+}]\) their concentrations in solution. If the same units are used to express the concentration of ions in the resin and in the solution, then \(K_c\) will be dimensionless, but its value will depend on the units employed.

### 7.6.2.2 Properties of Synthetic Ion-exchanger Resin

The properties of ion exchangers may be simplified to capacity, equilibrium properties, and kinetic behaviour since these criteria mainly determine the ion-exchange process. It is precisely the possibility of predetermining the properties of exchanger materials by their synthesis which has been the decisive factor in giving synthetic ion exchange resins their superior position compared to natural ion exchange materials.

These synthetic possibilities in themselves have the purpose of manufacturing products which always satisfy the objective, are of high quality, and, equally important, can be used economically.

#### 7.6.2.2.1 Moisture content and density.

Commercial ion exchanger materials have a certain moisture content in the form of bound water resulting from the hygroscopic properties of resin. Beyond this, ion exchangers can take up free water or surface water which can be removed as an unbound amount of water by drying and has no influence on the exchanger properties. The quantity of bound water depends on the nature, amount and form of functional groups, which have a positive influence on moisture uptake, and on the density of network formed by cross-linking between matrix molecules, permits a moisture uptake only until the osmotic forces are compensated.

The resulting moisture content is expressed in per cent of moisture per weight of wet resin, in per cent of moisture per weight of dry resin, or in weight or mole number of water per equivalent of exchange capacity.

The moisture content of Amberlyst 15 is maximum 1.5 % (per cent of moisture per weight of dry resin) as we can see on the process data sheet of Rohm and Haas [12](appendix A.7.VI) .
7.6.2.2.2 Particle size.

Ion exchange beads or granulates, such as Amberlyst 15, generally are marketed in particle sizes of between 0.3 - 1.2 mm [12]. The listed measure of particle size is the diameter in mm or according to standard screen sizes in "mesh" values. The American standard screen size (US mesh) can be converted into millimeters by the following rule:

\[
\frac{16}{\text{mesh}} = \text{particle diameter in mm}
\]

The ion exchange particles have a different volume in the dry and the wet states and therefore also have different particle sizes. This difference is due to the moisture holding capacity of the exchange resins and depends on the nature of functional group and the degree of cross-linking. In the column process, the dependence of the flow rate on particle size is most apparent. Since the frictional resistance is higher with smaller particle sizes, the flow rate also decreases with decreasing particle size. To prevent a complete holdup of the liquid to be filtered in the column, an overpressure must be applied on it by suitable device. The influence of particle size on the exchange rate can be seen in figure 7.14. The exchange rate will increase as the particle size decrease. The diffusion path length of the exchanging ions to and from the active sites are shorter with smaller particle size, so that exchange will more rapid.

7.6.2.2.3 Cross-linking.

The degree of spatial interlinkage of ion exchangers is determined by the production process. Commercial synthetic ion resins, such as Amberlyst 15, contain 8% divinylbenzene as a cross-linking agent [11]. Since cross-linking has a controlling influence on several properties of an exchanger, this step offers an opportunity in synthesis to produce special types of exchangers for special purposes. The cross-linking influences not only the solubility but the mechanical stability, exchange capacity, water uptake and swelling behavior, volume changes in different forms loading, selectivity, and chemical as well as oxidation resistance of ion exchangers. Exchangers with a low degree of cross-linking are soft and mechanically unstable (in the swollen state), while highly cross-linked products are hard and brittle. With a higher degree of cross-linking, the moisture content and swelling behavior of the exchanger decreases. The volume change of the loading form which changes during regeneration is greater with a lower than with a high degree of cross-linking. The selectivity increases with higher degree of cross-linking.

7.6.2.2.4 Porosity.

The porosity of ion exchanger resins is related to the degree of cross-linking and the network formed as a result. The porosity of Amberlyst 15 is equal to 0.40 ml volume per gram. The size of these capillary channels depends on the degree of cross-linking but is not uniform in one and the same ion exchange particle. The porosity also influences other ion-exchanger properties, mainly the capacity and selectivity. The capacity will be much
lower than it really is if the exchange resins have no pores and if only the functional
groups at the surface are active for ion exchange.

7.6.2.2.5 Swelling.

The volume of an ion exchanger depends on several factors: (1) the surrounding
medium (water, air, organic solvents), (2) the nature of the resin skeleton (type of
matrix and cross-linking), (3) the charge density (nature and concentration of ionic
groups), and (4) the type of counterions.
The volume change which takes place during transition from one medium into
another and which influenced by other factors is known as swelling.

7.6.2.2.6 Capacity.

The capacity is the most important property of an ion exchanger. It thus becomes
necessary to indicate the specific units and conditions when capacity are cited. For
laboratory and research purposes it has become increasingly popular to state the
capacity in milliequivalents per gram (meq/gram) or in milliequivalents per 100 gram
(meq/100 gram). The capacity of Amberlyst 15 is 4.7 meq/gram [12]. This is understood
to refer to cation exchangers in the H-form.

7.6.2.3 General Process Model Description

7.6.2.3.1 'Batch' process.

The ion exchanger is packed in a column and all necessary operations are carried out
in this bed, figure 7.15. If a packed column contains the ion exchanger with counterion
C¹, we are dealing with the equipment shown in part I of figure 7.16. The counterion
C¹ of an exchanger is to be exchanged for the counterion C² of a solution in a overhead
reservoir. As soon as solution with C² has entered the exchanger bed (figure 7.16, II),
C² ions are exchanged by the exchanger. After a short time, the exchanger in the upper
section of the column is completely loaded with C² as counterions. Additional C² ions
flow unhindered through this part of the bed and reach the exchange zone farther down,
where the C¹ counterions exchange sites quantitatively with the C² ions. The liberated
C¹ ions are eluted at the lower end of the column in a stoichiometric ratio. If this
process is continued, the exchange zone in the column continues migrate until it reaches
the lower end and the overall process has come to the point where C¹ and C² ions are
simultaneously eluted from the column. Breakthrough takes place, at which the
concentration of C² ions in the flow begins to increase prominently until it finally has
reached the same concentration as in the solution which was initially charged on the
column (figure 7.16, III). If the C² ions are charged once more (figure 7.16 IV), no
further ion exchange can take place, since the entire exchanger already has the C² form;
the C² ions flow through the column without hindrance. See figure 7.17.

7.6.2.3.2 'Continuous' process.

Continuous ion exchange processes are characterized by the simultaneous performance
of ion exchange and regeneration in different parts of the equipment. An ideal
continuous ion exchange will be designed in such a way that the consumed ion exchanger is continuously removed and transported to regeneration and freshly regenerated exchanger is supplied to the process. Such designs have been realized in water softening process.

7.6.3 Results

7.6.3.1 Results of the Removal of DADPM from Flexibles

7.6.3.1.1 Basic equation.

Adsorption :

\[ \text{H}_2\text{N-C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2 + 2(\text{R'}-\text{HSO}_3) \rightarrow \text{H}_2\text{N-C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2(\text{R'}-\text{HSO}_3)_2 \]

DADPM Amberlyst 15

Regeneration :

\[ \text{H}_2\text{N-C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2(\text{R'}-\text{HSO}_3)_2 + 2 \text{HCl} \rightarrow \text{H}_2\text{N-C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2(\text{HCl})_2 + 2\text{R'}-\text{HSO}_3 \]

7.6.3.1.2 The 'batch' process.

The design of column is based on the quantity of the Flexible stream, concentration and the capacity of resin. The batch process equipment consists of one column and one storage, see figure 7.18.

For the stream distributor in the column be used a spray tower via a manifold of nozzles.

The process is carried out in two steps:

1. The adsorption process
2. The regeneration process

The adsorption process;
The ion exchanger Amberlyst 15 serves for the removal of DADPM from Flexible. The Flexible stream contains a little DADPM and MEG. DADPM will be removed by ion exchanger Amberlyst 15. When Flexible is passed over the ion exchange bed (Amberlyst 15) in adsorption process, its DADPMs are bound by Amberlyst 15 and thus the Flexible contains only DADPM with content less than 20 ppm and MEG.
The column is dimensioned for one day adsorption process.
After the adsorption process the resin must be reactivated by the regeneration process.

The regeneration process;
During the regeneration process, the Flexible flows into the storage.
The Amberlyst 15 resin bed will be backwashed with water at such a rate that the bed volume increases by 50 percent. The bed allowed to classify while the backwash flow is maintained until rest of the flexible is removed. Ten percent HCl is now passed downflow through the Amberlyst 15 bed at a rate of 4 bed volumes per hour until a total of 1.5 bed volumes of HCl has passed through the column.
De-ionized or distilled water will be used for rinsing excess regenerant (HCl) from the column, with the initial flow rate the same as the regeneration flow rate until about one to two bed volumes of rinse water has passed through the column. After the displacement rinse, the rinse flow rate with deionized or distilled water will be increased to 12 bed volumes per hour and continued until the effluent has a pH above 4. A minimum of three bed volumes of water rinse is usually required. After Amberlyst 15 has been drained free of water, it may be dried by air-drying (105 °C).

7.6.3.1.3 The 'continuous' process.

The continuous process equipment consists of the packed columns that parallel be coupled and work interaction, see figure 7.19. The reason of this design is the Flexible may be not mixed with water.
The adsorption and regeneration processes are the same as by the batch process.
The advantages of the continuous process:
- The Flexible stream can be treated continuously
- On the basis of the cost estimation, the continuous process is more favourable than the batch process.

7.6.3.2 Calculation of Column Dimensions

The bed volume in the column

\[ V_{\text{bed}} = A_o l (1 - e) \]  

where \( V_{\text{bed}} \) is volume of bed
\( A_o \) is total cross-sectional area of bed or column
From appendix 1; \( V_{\text{bed}} = 0.011 \text{ m}^3 \).

The stay time of Flexible over the bed:

\[ T = \frac{l}{u_1} \]  

where \( l \) is the thickness of the bed
\( u_1 \) is average velocity through the pore channels

From appendix A.7.VI; \( T = 33.4 \text{ seconds.} \)

The pressure drop across granular bed

The flow of fluid through bed composed of stationary granular particles is a frequent occurrence in the chemical industry and therefore expressions are needed to predict pressure drop across beds due to the resistance caused by the presence of the particles. The drop in pressure for flow through a bed of small particles provides a convenient method for obtaining a measure of the external surface area of a powder, for example pigment.

The average velocity over whole area of bed can be written, Darcy’s Law, as follows:
where \(-\Delta P\) is the pressure drop across the bed,
\(u\) is the average velocity of flow of the fluid,
\(K\) is a constant depending on the physical properties of the bed and fluid.

The resistance to flow then arises mainly from viscous drag. And then can be expressed as:

\[
u = K \frac{(-\Delta P)}{l} = B \frac{(-\Delta P)}{\mu l}
\] (7,19)

where \(\mu\) is the viscosity of the fluid and \(B\) is termed the permeability coefficient for the bed, and depends only on the properties of the bed.

The value of the permeability coefficient is frequently used to give an indication of the ease of passing a fluid through bed of particles [14].

The general structure of a bed of particles can be often be characterised by the specific surface area of the bed \(S_B\) and the fractional voidage of the bed \(e\).

\(S_B\) is the surface area presented to the fluid per unit volume of bed when the particles are packed in a bed. Its units are \((\text{length})^{-1}\).

\(e\) is the fraction of the volume of the bed not occupied by solid material and is termed the fractional voidage, voidage, or porosity. It is dimensionless. Thus the fractional volume of the bed occupied by solid material is \((1 - e)\).

\(S\) is the specific surface area of the particles and is the surface area of a particle divided by its volume. Its units are again \((\text{length})^{-1}\). For a sphere:

\[
S = \frac{\pi d^2}{\pi (d^3/6)} = \frac{6}{d}
\] (7,20)

It can be seen that \(S\) and \(S_B\) are not equal due to the voidage occurring when the particles are packed into a bed. If point contact occurs between particles so that only a very small fraction of surface area is lost by overlapping, then:

\[
S_B = S (1 - e)
\] (7,21)

A shape of particle \(S\) increases as the particle size is reduced. As \(e\) is increased, flow through the bed becomes easier and so the permeability coefficient \(B\) increases.

The analogy between streamline flow through a tube and streamline flow through the pores in a bed of particles is a useful for deriving a general expression.
The equation for streamline flow through a circular tube is:

\[ u_t = \frac{d_t}{32\mu} \left(\frac{-\Delta P}{l_t}\right) \]  

(7,22)

where \( \mu \) is the viscosity of the fluid,
\( u_t \) is the mean velocity of the fluid,
\( d_t \) is the diameter of the tube, and
\( l_t \) is the length of the tube.

If the free space in the bed is assumed to consist of a series of tortuous channels, equation for flow through a bed may be written as:

\[ u'_t = \frac{d_m^2}{K'\mu} \left(\frac{-\Delta P}{l'}\right) \]  

(7,23)

where \( d_m \) is some equivalent diameter of the pore channels, \( K' \) is a dimensionless constant whose value depends on the structure of the bed, \( l' \) is the length of channel, and \( u_t \) is average velocity through the pore channels.

It should be noted that \( u_t \) and \( l' \) represent conditions in the pores and are not the same as \( u \) and \( l \). However, it is a reasonable assumption that \( l' \) is directly proportional to \( l \).

Also, in [14] relate \( u \) and \( u_t \) by the following argument:

In a cube of side \( X \), the volume of free space is \( eX^3 \) so that the mean cross-sectional area for flow is the free volume divided by the height, or \( eX^2 \).

The volume flow rate through this cube is \( uX^2 \), so that the average linear velocity through the pores, \( u_t \), is given by:

\[ u_t = \frac{uX^2}{eX^2} = \frac{u}{e} \]  

(7,24)

Thus with a bed of spheres arranged in cubic packing, \( e = 0.4 \).

The equivalent diameter of the pore space is proposed in [14] that \( d_m \) can be taken as:

\[ d_m = \frac{e}{S_B} = \frac{e}{S(1-e)} \]  

(7,25)

where \( e/S_B = 1/4 \times \) hydraulic mean diameter.
The modified Reynolds number $Re_i$ is obtained by taking the same velocity and characteristic linear dimension $d_w$. Thus:

\[
Re_i = \frac{u_i e}{\rho S(1-e) \mu} \quad (7.26)
\]

The friction factor, which is plotted against the modified Reynolds number, is $R_i/\rho u_i^2$, in figure 7.20, where $R_i$ is the component drag force per unit area of particle surface in the direction of motion. $R_i$ can be related to the properties of unit cross-sectional area and thickness $l$. The volume particles in the bed is $l(1 - e)$ and therefore the total surface is $S(l - e)$. Thus the resistance force $= R_i S(l - e)$. This force on the fluid must be equal to that produced by pressure difference of $\Delta P$ across the bed. Then, since the free cross-section of fluid is equal to $e$:

\[
(-\Delta P).e = R_i S(l(1-e))
\]

and

\[
R_i = \frac{e (-\Delta P)}{S(1-e) l}
\]

Thus

\[
\frac{R_i}{\rho u_i^2} = \frac{e^3 (-\Delta P)}{S(1-e) l \rho u^2}
\]

From curve A in figure 7.20, for the flow through randomly packed beds of solid particles can be correlated approximately:

\[
\frac{R_i}{\rho u_i^2} = 5Re_i^{(-1)} + 0.4Re_i^{(-0.1)}
\]

Comparison with equation 7.26 shows that $(-\Delta P)$ the pressure drop is given. From appendix A.7.VII, the pressure drop is equal to 2.297 bar.

### 7.6.3.3 Cost Estimation

The cost estimation of equipments of batch and continuous processes are:

The cost of batch process:

The batch process consists of storage (3 m³) and the column (bed volume $= 0.011$ m³).
The cost of storage can be estimated from [15]:
The equation:
\[ C_e = C \cdot S^n \]
where
- \( C_e \) is purchased equipment cost, £,
- \( S \) is cost constant,
- \( n \) is index for that type of equipment.

For the carbon steel storage with capacity 1 - 50 m³ at atmospheric pressure: \( C = £. 500.-- \); \( S = 3 \); \( n = 0.59 \).
Substitute the values into the equation, the cost of storage is £. 956.--.

The cost of storage in guilders is fl. 3,346.--
The cost of cation exchanger (Amberlyst 15) is fl. 79.80 per litre. The total cost of bed is fl. 877.80. And because the column dimension is small there is no specification in the literature.
Thus the total cost of column can be estimated only from the cost of the bed.

The cost of pump [10]:
specification:
- pump capacity = 12.5 m³/h.
- power = 1.1 kW.
- DIN 24255
- iron
- electro motor: temperature operation: 200 °C.
- class: IPA54.
- power = 1.1 kW.

The total cost of pump is the cost of the pump material plus the cost of electro motor is equal to fl. 1,750.-- + fl. 410.-- = fl. 2,160.--.

The total cost of batch process is equal to the cost of storage plus of the column bed, thus fl. 3,346.-- + fl. 877.80 + fl. 2,160.-- = fl. 6,383.80.

The cost of continuous process:
The continuous process consists of two identical column with the bed volume 0.11 m³. And because the column dimension is small there is no specification in the literature.
The total cost of column can be estimated only from the cost of the bed.
Thus the total cost of continuous process is the total cost of column plus the total cost of pump.
The total cost of continuous process is equal to fl. 1,755.60 + fl. 2,160.-- = fl. 3,195.60

7.6.4 Conclusion

The continuous process of the ion exchanger is the best process for the removal of DADPM from Flexible.
7.7 Literature


8 CONCLUSIONS AND RECOMMENDATIONS

Again a differentiation in feed, reaction and work-up section is made.

A dispersion of 1000 kg/h PU in 10,000 kg/h MEG should be made. This MEG/PU ratio is required in order to make transport of the dispersion possible by pumping. A suitable feed system is the 'flash option'. This option contains two cutters in series, cutting the crude PU. After that the dispersion is made in a mixing vessel with an in line high shear mixer, followed by a flash which removes the water out of the dispersion. Finally the dispersion is preheated to 200°C and transported to the reactor. Main advantages of this option are:

1. lowest investments costs;
2. very flexible water removal process;
3. the specifications will be met quite easy.

Conservative estimation/calculations resulted in an oversized main reactor system. For more accurate design, more detailed data of the reaction kinetics are required. The reactor system as designed consists of two equal CSTR's (25 m³) in series with a filter placed in between. The filter controls the maximum of particles in the reactors effluent. In the first reactor nearly all PU is converted. The second reactor is required to break down the PU to molecular dimensions. If a filter with smaller perforations is used, smaller volumina are sufficient.

As far as reaction kinetics are concerned less MEG can be used in the reactor. Because the transport from feed section to reactor requires a MEG/PU ratio of 10, a large separation units are needed. If mixing, flashing and reaction are performed in the same vessel, there is no transport problem, less MEG is required and smaller separation units can be used. This alternative will have to be operated batchwise. The effluent of the reactor can be separated quite well in a settler. This should be a horizontal vessel of 2.5 m length and 0.4 m diameter.

The separation column to separate the crude MEG from the Rigids (calculated for the MEG/PU ratio of 10) has to be a distillation column with 10 theoretical trays. This results in a sieve trays column of 10 metres length and 1.50 m diameter or a packed column with a length of 7.60 m and a diameter of 1.36 m. The large amount of heat released in the condensor should be used for instance to heat up oil as this heat can't be used elsewhere in the process.

To remove the largest amount of DADPM from the flexible stream, coming from the settler, we find the RDC extractor to be the best solution, at a temperature of 80°C. This extractor has a total length of 10 m and a diameter of 0.40 m.

To separate the MEG from the flexibles an adiabatic flash at a feed temperature of 200°C and pressure of 1.0 bar has turned out to be the best separator, because: it's most easy to control, requires less vacuum and it's cheap.

DADPM is removed from the flexibles by processing the stream in a fixed-bed ion-exchanger with Amberlyst 15 as resin. The design of two columns parallel, characterized by the simultaneous performance of ion exchange and regeneration in different parts of the equipment, is to be preferred.