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Recycling of by-products from formalin production by introduction of a new absorption unit

Master of Science Thesis

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Abstract

In the production of formalin the main cost is that of the raw material methanol and therefore a high yield is essential. In the Formox-process (developed and sold by Formox AB), a gas stream holding dimethyl ether, methanol and formaldehyde is presently oxidised in a total oxidising reactor. In this study we investigate if these components can be recovered and recycled and if such a procedure is economically feasible. The study focuses on dimethyl ether because of its larger quantity in the gas stream compared with the other two components. The study was made at Formox AB.

The absorbability of dimethyl ether was investigated with theoretical calculations, calculations based on literature data and experiments. The theoretical results and the literature data were in agreement while the experimental results showed a slightly lower absorbability but in the same order of magnitude. 0.21% dimethyl ether absorbed in the theoretical and literature based calculations and 0.18% in the experiments.

The effect on the absorbability of dimethyl ether by addition of methanol and formaldehyde was investigated and was found not to be significant at the concentrations used. Theoretical calculations were made for methanol and compared to simulated results but no experiments done. The simulations were made in CHEMCAD of an absorption unit and the results (0.23% absorption of dimethyl ether, 24.91% absorption of methanol and 100% absorption of Formaldehyde in the best case scenario) were used in a mole balance to estimate the possible savings.

A basic design was made based on a sizing made in CHEMCAD, guide lines from literature and advice from Process Engineers at Formox AB.

It was found that the profitability of a new absorber was low; a payback period of 12 years and a positive Net Present Worth after 19 years for the best case scenario. Since the profitability was also found to be highly dependent on the raw material price and the steam price, it is not an advisable investment. The results should be viewed as a first insight into the usefulness of a new absorber baring in mind the sources of error (e.g. CHEMCAD which cannot estimate the interactions of all components together and cannot estimate temperature dependencies for the absorbability of the components).

It was found that recovery of methanol and formaldehyde can be interesting but more research is needed to produce a better estimate of the absorbabilities of these two components.

Keywords: Dimethyl ether, Absorber, Methanol, Formaldehyde, Economic Evaluation, CHEMCAD

Table of Contents

1	INTRODUCTION	1
2	THEORY	3
2.1	Absorption	3
2.2	Thermodynamic models	4
2.2.1	Henry's law	4
2.2.2	PSRK model.....	5
2.2.3	Maurer model	5
2.2.4	UNIFAC model	5
2.2.5	Wilson model	5
2.3	Choice of thermodynamic model	6
2.4	Chemical species of interest	6
2.4.1	Methanol	6
2.4.2	Dimethyl ether.....	6
2.4.3	Formaldehyde.....	7
3	METHOD.....	8
3.1	Degree of absorption	8
3.2	Theoretical calculations	8
3.3	Calculations based on literature data	8
3.4	Basic simulation of a single unit	8
3.5	Experiments.....	9
3.5.1	Experimental procedure	10
3.5.2	Interpretation of results	12
3.6	Advanced simulation of single unit.....	13
3.7	Design and cost estimation.....	14
3.7.1	Investment estimation	15
3.7.2	Savings estimation	15
3.7.3	Economics.....	16
3.8	Sensitivity analysis	17
4	RESULTS AND DISCUSSION.....	18
4.1	Degree of absorption results.....	18
4.1.1	Henry's law	18
4.1.2	Literature data	18
4.1.3	Experimental data	18
4.1.4	Basic simulation data	20
4.2	Results from advanced simulations.....	21
4.2.1	Absorber.....	21

4.2.2	ECS-model	22
4.3	Results from the savings estimation	23
4.4	Results from the economic evaluation	23
4.4.1	Investment	23
4.4.2	Economics	24
4.5	Sensitivity analysis	25
5	CONCLUSIONS	26
5.1	Absorbability of dimethyl ether	26
5.2	Simulation	26
5.3	Economic evaluation	26
5.4	Summary	27
6	ACKNOWLEDGEMENTS	28
7	BIBLIOGRAPHY	29
Appendix 1. Chart for choosing thermodynamic model		
Appendix 2. Basic sketch of the new absorption unit		
Appendix 3. Explanations of the savings estimation		
Appendix 4. Vapour pressure data of DME from three sources		
Appendix 5. Vapour-Liquid equilibrium data from the DME-water system at four temperatures		
Appendix 6. Chromatograms from experiments		
Appendix 7. The dependency of DME and MeOH absorption on number of stages		
Appendix 8. Plots of experimental results		
Appendix 9. Sensitivity analysis plots		

1 INTRODUCTION

Formalin, which is the commercial name for a solution of formaldehyde and water, is mainly used to produce products such as glue and specialty chemicals [1]. The Formox-process is a process for formalin production developed and sold by Formox AB. As shown in Figure 1, methanol (MeOH) is oxidised to formaldehyde (FA) with dimethyl ether (DME) and carbon monoxide (CO) being formed as main by-products. Most of the formaldehyde is then absorbed in two absorption units, placed on top of each other forming only one tower, while the by-products are partly recycled (around 2/3) and partly incinerated into carbon dioxide in a total oxidising reactor, called Emission Control System (ECS). Considering that the methanol cost represents some 93% of the production cost, a high yield is essential for the profitability of the process. In this study, which was made at Formox AB, the potential to increase the plant yield by recovering MeOH, DME and FA from the stream going to the ECS was evaluated. Here the first two components can be oxidised to FA in the main reactor while the FA in the stream can be led down to the absorption units and from there end up in the product stream. As mentioned above, the reaction of MeOH creates both DME and CO as by-products but by adjusting the catalyst loading profiles it may be shifted, to some extent, to increase the production of DME and decrease the production of CO. This would be interesting since CO cannot be reacted into formaldehyde in the Formox-process. The stream which is to be recycled holds much more DME than it does MeOH or FA. Because of this the potential yield increase is higher for recovering DME than it is for recovering MeOH or FA.

Since many plants built by Formox operate at considerably higher capacities than what they were designed for, the ECS can become a bottleneck in obtaining higher productivity because it is sensitive to high temperatures. Therefore a further benefit of recycling material from the stream going to the ECS would be that the heat generated in the ECS would be lowered [2].

The purpose of the study was to technically and economically evaluate the possibility to absorb DME, MeOH and FA by water in a new absorption unit positioned before the ECS. The process water used in this unit could then be used in the existing absorption units. The evaluation of a new absorption unit consisted of simulations of the new unit along with the ECS for a generic version of the Formox-process (where the compositions of the streams in Figure 1 are known). The rest of the process was not simulated. A basic design of the new unit was made. Experiments on the absorbability of DME in water were made with and without addition of MeOH and FA to investigate their effect on the absorbability.

In Figure 1 below a schematic of the Formox-process is shown. The unit marked A3 represents the new possible absorption unit.

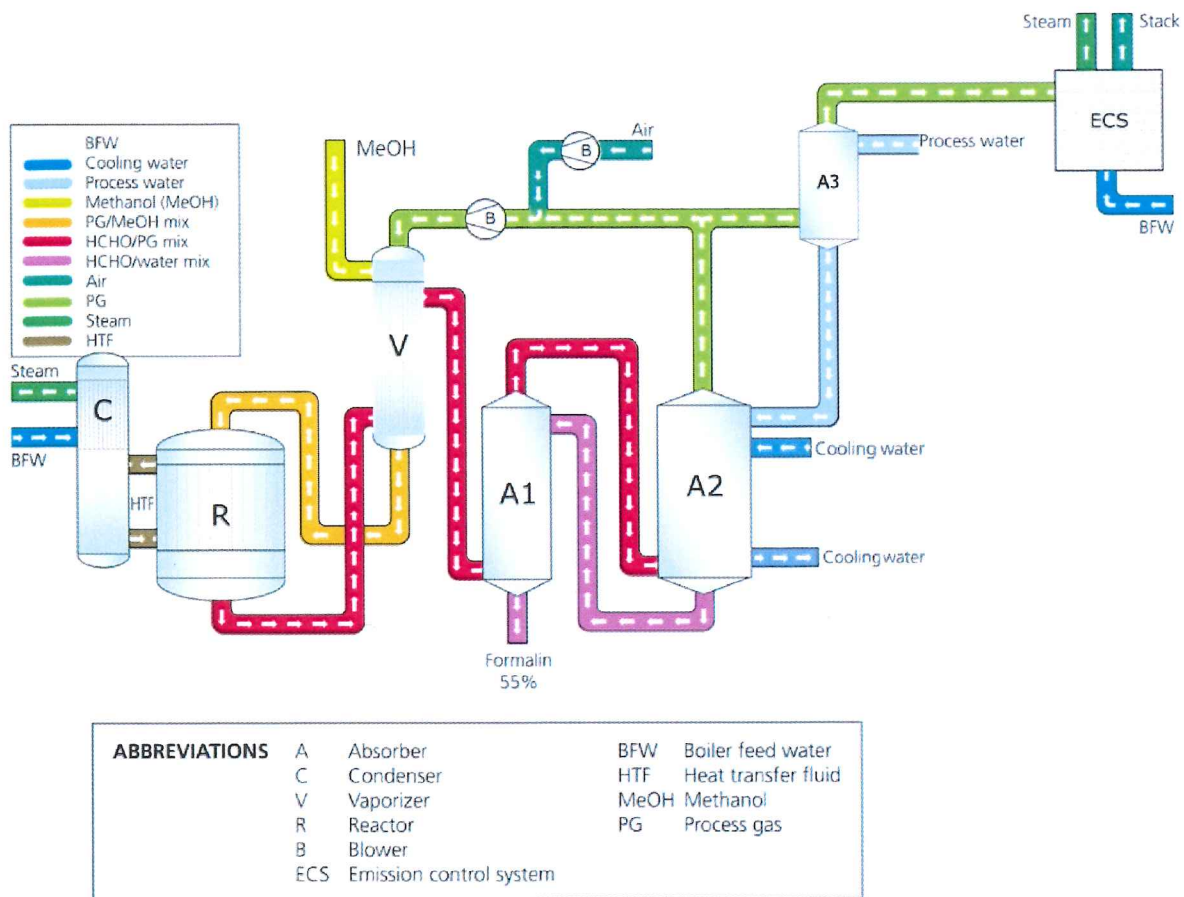


Figure 1. Schematic of the Formox-process along with the possible new absorption unit marked A3 [3].

2 THEORY

2.1 Absorption

Absorption is the physical equilibrium process of dissolving gaseous components in a liquid by putting the two phases in contact with each other. Absorption is similar to distillation and stripping (also called desorption). In distillation mass transport takes place from both the gaseous and the liquid phases, while in absorption mass transport only takes place from the gaseous phase to the liquid phase and the other way around for desorption.

Industrial absorption is generally carried out in columns with either trays or packing material, although other equipments exist such as spray towers or bubble columns [4].

To calculate the composition of either phase at equilibrium, phase equilibrium ratios or, as they are also called, K-values are used. These values are the ratio between the amounts (in moles or kg etc) of a component in each phase at equilibrium, y_i for the gaseous phase and x_i for the liquid phase as shown in equation 1 below.

$$K_i = \frac{y_i}{x_i} \quad (1)$$

K-values only describe the equilibrium of the system and do not take mass transport resistances into account. By describing a system with the two film theory, as seen in Figure 2, the K-value only describe the transport from the gaseous film to the liquid film. Transport resistances occur in the bulks, the films and between the bulks and the films of the phases.

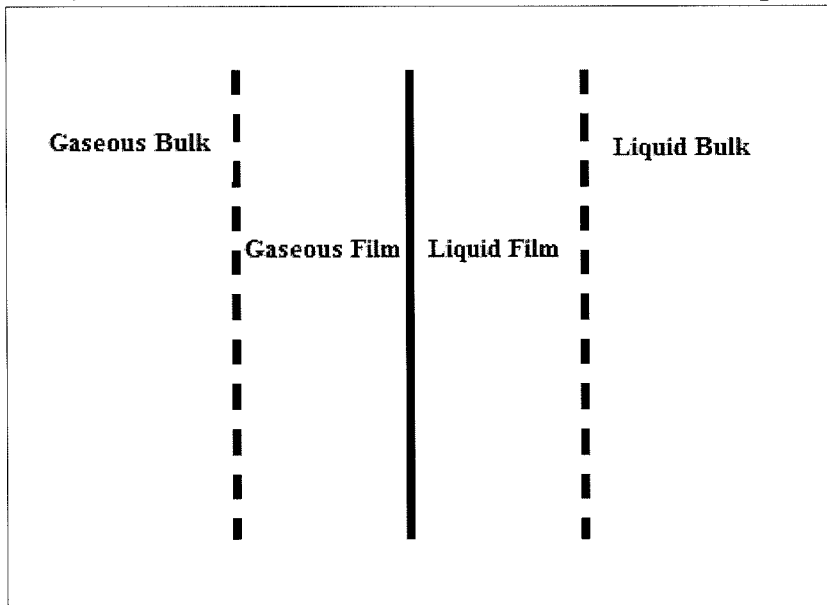


Figure 2. Illustration of the two-film theory

There are many models used to estimate K-values such as Henry's law, the PSRK (Predictive Soave-Redlich-Kwong) model or the Wilson model. These models are often called K-value models or thermodynamic models and most models are either equation-of-state based or activity coefficient based. The equation-of-state approach uses the partial fugacities of the components in each phase to describe the ratios. The activity coefficient approach uses activity coefficients along with fugacities. The choice of thermodynamic model depends on the components in and on the knowledge of system of interest as described below in section 2.3 [5].

2.2 Thermodynamic models

Five models were investigated in the study. The three models mainly used were Henry's law, the PSRK model and The Maurer model. Below are descriptions of each model and in Table 1 their area of use and downsides are summarised.

2.2.1 Henry's law

Formulated by the British chemist William Henry, Henry's law states that the amount of a component in the gaseous phase is proportional to the amount of that component in the liquid phase of the system by a constant, the Henry constant (k_H), specific for the system of interest.

Henry's law is viable for low concentrations of the component of interest at low pressures since it is based on the assumption that the molecules of the component only interact with molecules of the solvent [6]. Henry's law can be formulated in different ways, with one version shown below in equation 2 where p_i is the partial pressure and n_i is the molar amount of component i in the liquid phase.

$$p_i * k_H = n_i \quad (2)$$

In this formulation the Henry constant can be regarded as the K-value.

The Henry constant is highly temperature dependent and to account for this an equation was developed to calculate the Henry constant at a specific temperature by using the constant at a well known temperature, as described in [7]. Equation 3 illustrates this method, where k_H is the Henry constant, k_H^0 is the Henry constant at the reference temperature, ΔH_{soln} is the solution enthalpy, T is the temperature and R is the gas constant.

$$k_H = k_H^0 \times \exp\left(\frac{-\Delta H_{soln}}{R} \left(\frac{1}{T} - \frac{1}{T^0}\right)\right) \quad (3)$$

Equation 4 is called the Van't Hoff equation and it is the slope of how the equilibrium constant depends on the temperature. It is not restricted to physical equilibrium but applies for chemical equilibrium as well [7, 8]. Values to use in Equation 3 are constants that equal the left hand side of the Van't Hoff equation and are available for many systems.

$$\frac{-d \ln k_H}{d(1/T)} = \frac{-\Delta H_{soln}}{R} \quad (4)$$

As described in [9] the Henry constant can for any given temperature be re-calculated from the constant at a reference temperature. The Henry constant can be described as in Equation 5.

$$k_H = \gamma^{inf} p^{vap} \quad (5)$$

Where γ^{inf} is the activity coefficient at infinite dilution and p^{vap} is the vapour pressure of the pure component at the given temperature. It is stated that the contribution of the activity coefficient is small when comparing the Henry constants at two temperatures, if the temperature interval is not too large, and because of this the Henry constants can be described as shown in equation 6.

$$\frac{k_H}{k_H^{ref}} \approx \frac{p^{vap}}{p^{vap,ref}} \quad (6)$$

Equation 6 is applicable as shown when the unit of k_H is purely pressure, for example Pa. In this

thesis the unit of k_H is $\text{mol/m}^3\text{Pa}$ which means that equation 6 has to be slightly modified to apply. Since the pressure is in the denominator in the unit the equation must be changed as shown below [9].

$$\frac{k_H}{k_H^{ref}} \approx \frac{\left(\frac{1}{p^{vap}}\right)}{\left(\frac{1}{p^{vapref}}\right)} = \frac{p^{vapref}}{p^{vap}} \quad (7)$$

2.2.2 PSRK model

PSRK stands for Predictive Soave-Redlich-Kwong and it is an equation-of-state model. Two Chemical engineers, Redlich and Kwong, developed a simple equation-of-state model called the Redlich-Kwong model (R-K). It was later modified by Soave and the modified model was called the Soave-Redlich-Kwong model (S-R-K). The SRK model was combined with the UNIFAC by Holderbaum and Gmehling and they further enhanced the temperature dependencies. The model was developed to be able to estimate systems containing both polar compounds and supercritical compounds (light gases) where the SRK and the UNIFAC models were lacking [5].

2.2.3 Maurer model

In this thesis the Maurer model refers to the model in CHEMCAD with the same name. The model is based on the work in [10] and was developed for simulations of the FA-MeOH-water systems in CHEMCAD. As described in [11], it combines equilibrium reactions in the system with an activity based model (UNIFAC), thus it can be seen as such a model. The nature of FA is very complex and most thermodynamic models cannot provide reliable estimates of systems containing the component, thus the need of this particular model.

2.2.4 UNIFAC model

The UNIFAC model is an activity coefficient based model. It uses functional groups to estimate activity coefficients for the liquid phase instead of using vapour-liquid equilibrium data as a basis. The functional groups are groups of atoms in the molecules which give different interactions depending on which atoms that are present in the group. An example of a functional group is a hydroxyl-group, -OH. The model is built on another activity coefficient based model which is called UNIQUAC (Universal quasi-chemical). The UNIFAC model is useful for unexplored mixtures since it does not need vapour-liquid equilibrium data. It is also suitable for polar components [5].

2.2.5 Wilson model

The Wilson model (sometimes referred to as the Wilson equation) is an activity based model which uses binary interaction parameters (BIP) to estimate binary systems. Multi-component systems are treated as many pseudo-binary systems. The model works well for non-ideal dilute systems of components that are miscible [5].

Table 1. Summary of the Thermodynamic models used in the study [5, 11]

Thermodynamic model	Area of usage	Downsides
Henry's law	Simple to use and applies for most systems	Only suitable for well known dilute systems
PSRK	Suitable for polar and/or supercritical components of unknown systems	Requires data on functional groups to be accurate
Maurer	Used specifically for the MeOH-FA-water system	Complex model only suitable for the MeOH-FA-water system
UNIFAC	Suitable for polar components of unknown systems	Requires data on functional groups to be accurate
Wilson	Suitable for non-ideal miscible systems of which BIPs are known	Not suited for unknown systems without BIP data

2.3 Choice of thermodynamic model

When simulating chemical processes the choice of thermodynamic model (K-value model), used to describe interactions between components, is very important if reliable results are to be obtained. A poor choice of thermodynamic model can often give very inaccurate results.

In the literature suggestions can be found on how to choose a model, provided in [5] and in [12]. Suggestions from the latter are provided in Appendix 1. In many flow sheeting software a built-in function is provided which gives a suggested model based on the specified components. The components in the simulations are listed in Table 9.

For our system, the components of highest interest are polar, of which three are hydrocarbons. Supercritical compounds are present such as CO and Nitrogen. By following the path in the figure in Appendix 1. Chart for choosing thermodynamic model we will choose the UNIFAC model since the supercritical components are not regarded in that figure. According to [5] the PSRK model should be used for systems containing polar components and supercritical components. For systems where there are no supercritical components present, the UNIFAC model should be used unless there are BIPs available for the system. If so, the Wilson model may be suitable [5].

If all components are used in the flow sheeting software CHEMCAD the suggested model is the Maurer model. This is because of the presence of formaldehyde which, as stated above, shows a very complex behaviour. If formaldehyde is omitted, CHEMCAD suggests the UNIFAC model.

2.4 Chemical species of interest

MeOH, DME and FA are the species investigated in the thesis due to their parts in the Formox-process, described in the background section.

2.4.1 Methanol

MeOH is the simplest of the alcohols and consists of one methyl-group and one hydroxide-group. At atmospheric pressure it boils at 64.7°C. It is slightly polar and miscible in water.

MeOH is often produced from natural gas via synthesis gas but other methods exist such as production from coal. It is used in many different ways for example as a solvent, as fuel or as raw material in industrial chemistry [13].

Vapour-liquid equilibrium data for the binary system of MeOH-water are available for higher temperatures but data for temperatures under 25°C are rare if available at all [14]. Henry's law data and temperature dependency data are available for the MeOH-water system [7].

2.4.2 Dimethyl ether

DME is the simplest ether consisting of two methyl-groups which are bonded in an ether-bond with oxygen. It is a volatile compound with a boiling point of -23.6°C at atmospheric pressure.[15] DME is slightly polar but sparingly soluble in water.

Vapour-liquid equilibrium data for the binary system of dimethyl ether-water are scarce but the work by [16] includes such data. Some vapour-liquid equilibrium data of ternary mixtures of the system DME-MeOH-water suggest that the solubility of DME gas is enhanced by the addition of MeOH [17].

A value of the Henry constant is available for the system DME-water system. There were no temperature dependencies for the Henry constant found in the literature [7].

2.4.3 Formaldehyde

FA is the simplest aldehyde consisting of a carbonyl-group bonded with two hydrogen atoms. It is a volatile compound with a boiling point of -21°C [18] and it is both very polar and very soluble in water.

Vapour-liquid equilibrium data are available but is a bit unreliable due to the complex nature of FA as mentioned above in section 2.2.3 and in [10]. Henry's law data are available for FA but these data have not been used in this study [7].

3 METHOD

3.1 Degree of absorption

In order to determine the potential of the absorption unit the maximum degree of absorption of DME (and to some extent MeOH) was determined using both theoretical calculations and experimental data. Degrees of absorption were estimated theoretically, calculated from vapour-liquid equilibrium data found in literature, simulated in a flow sheeting software (CHEMCAD version 6.2.0.3348) and calculated from experimental data. This was done for the temperatures 0°C, 10°C, 20°C, 25°C and 30°C for the theoretical and literature calculations and for 15°C, 20°C and 25°C for the experiments.

3.2 Theoretical calculations

The degree of absorption was calculated for the systems methanol-water and dimethyl ether-water using Henry's law. For the MeOH-water system calculations were straight forward with data for both the Henry constant and the terms in the Van't Hoff equation available [7]. The equation used was a combination of equation 3 and 4 shown as equation 8 below.

$$k_H = k_H^0 \times \exp\left(\frac{-d \ln k_H}{d(1/T)}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right) \quad (8)$$

For the FA-water systems there were terms available but they were deemed unreliable, as described in [10], and were therefore not used.

For the DME-water system, there were no data available for the terms in the Van't Hoff equation but a value for the Henry constant at 25°C was found [7]. As described above in section 2.2.1 Henry constants could be calculated by using the vapour pressure of DME at the temperatures of interest, as seen in equation 5. The vapour pressure data were taken from [19] and after comparing with similar data from [20] and [21] they were deemed reliable. The data was interpolated to be valid for the 25°C to use with the reference Henry constant, otherwise the data were unchanged.

3.3 Calculations based on literature data

The vapour-liquid equilibrium data of the DME-water system reported in [16] were used to find a degree of absorption for DME in water. Data near the temperatures of interest were plotted. By eliminating the data points at higher DME concentrations the data appeared linear and by introducing linear trend lines going through the origin for each temperature, K-values were obtained.

3.4 Basic simulation of a single unit

The basic simulation was made to try out different thermodynamic models and the results would then be compared with those from the theoretical and literature calculations as well as with the experimental data.

The simulation flow sheet consisted of a tower unit with two inlet streams and two product streams, see Figure 3. 200 stages were used to get values very close to the equilibrium of the systems. A process water flow of 44kmol/h was used in the simulations while the flow of process water is 59kmol/h in real plants of the type that was regarded in this study. This modification was made so that the process water stream from the new unit would not become too large since water in the gas stream would condense, adding to the liquid stream. Although the additional water did not increase the liquid flow to above 59kmol/h, the flow of 44kmol/h was still used.

Five different temperatures and four different thermodynamic models were used on a process where all components given in Table 9 were present. The models and the temperatures are shown in Table 2 and Table 3. The choice of models that were investigated was motivated as described in section 2.3. The Wilson model did not have any data on the DME-water system but TPx-data (Temperature, pressure and composition) could be inserted to get BIPs (Binary interaction parameters) for the system. The same data used in the calculations based on the literature data from [16] were put into CHEMCAD and new BIPs were regressed. No functional groups for FA to use in the UNIFAC model and the PSRK model were available in CHEMCAD but no additional data were inserted to account for that problem.

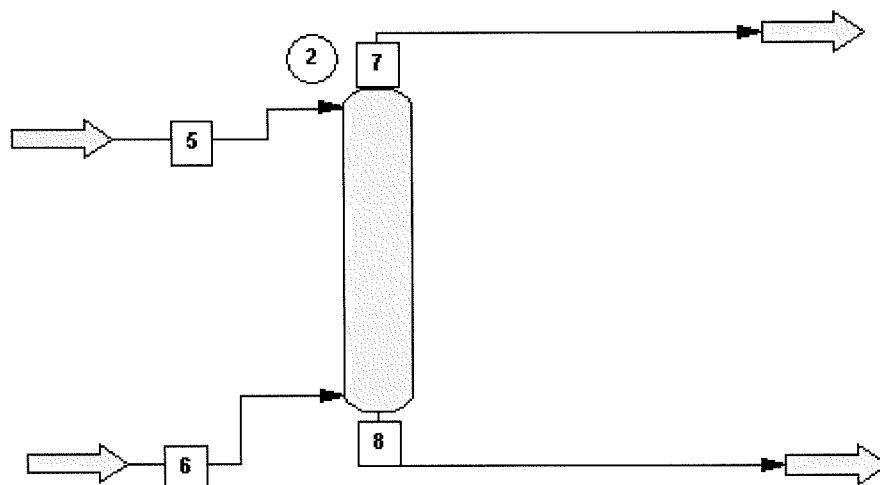


Figure 3. Flow sheet used for the basic simulations

Table 2. Temperatures of the process water investigated in the basic simulations

Temperature [°C]	0	10	20	25	30
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Table 3. Models investigated in the basic simulations

Model	PSRK	Maurer	UNIFAC	Wilson
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3.5 Experiments

Table 4. Material used in the experiments

Material
Nitrogen gas (as carrier gas)
Deionised water (absorbent)
Dimethyl ether (g)
Methanol (l)
Formaldehyde in 47% water solution

Table 5. Equipment used in the experiments

Experimental equipment
Mass Flow regulators, 0.02-0.2nL/min and 0.1-1.0nL/min
Water bath
Gas flow meter
Thermo couples
Gas chromatograph
Syringe pump

3.5.1 Experimental procedure

Gas was lead down into water in a container and the outlet gas was measured with a gas chromatograph able to detect dimethyl ether, methanol, formaldehyde and water. The basis for the experiments was that as the components are bubbled in the water they are absorbed which decreases the absorbability of the component until saturation is achieved. If plotted with time as the x-axis and amount of the component in the gas as the y-axis it would look as in Figure 4. By integrating the resulting curve with regard to time, and comparing this with how much would be transported in the gas over the same time interval if no absorption took place a total amount of how much was absorbed in the liquid could be obtained. This is also illustrated in Figure 4.

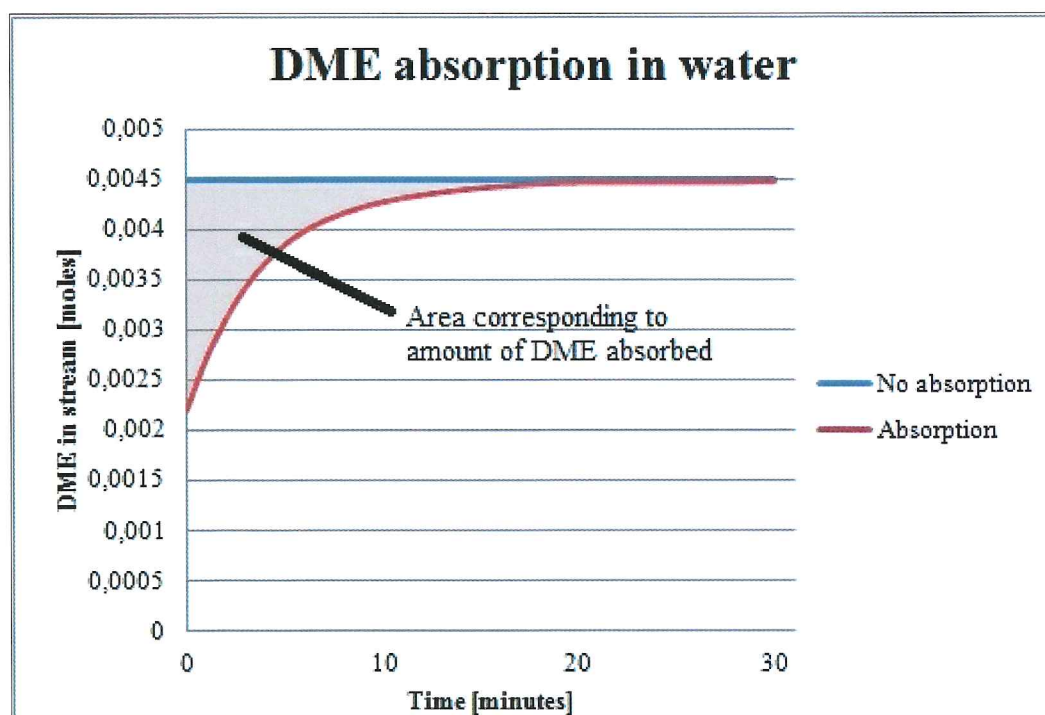


Figure 4. Illustration of the basis of the experiments

The gas flow was calibrated to get around 8.2nL/min (normal litres) of carrier gas (Nitrogen) and 0.1nL/min of DME. This was made with inert glass pearls to have the same volume in the vessel but without having to use water, which the gas meter was sensitive to. From the flows calibrated, (mentioned above) the amount of MeOH or MeOH-FA-water solution, to be injected with a syringe pump, was calculated to get same ratios as in the stream going to the ECS, compositions given in Table 9. The amounts of methanol and FA-water solution are given in Table 6. For the experiments without addition of FA, 0.06 ml/min of MeOH was injected while for the experiments with FA and MeOH the total 0.08 ml/min was injected.

Table 6. Volume of MeOH and FA injected in the experiments

MeOH	FA+H ₂ O	Total	
0.06	0.02	0.08	ml/min

The chromatograph took measurements every two minutes and the area of the peaks given in the chromatogram could be converted into mole percent.

The water used as absorbent was cooled to the temperature of interest and maintained at that temperature in a water bath assisted with ice packs as the temperature of the bath water was monitored with thermocouples. The water in the absorbing vessel was not monitored during the experiments.

A schematic of the setup is displayed in Figure 5 and pictures of the actual one is displayed in Figure 6.

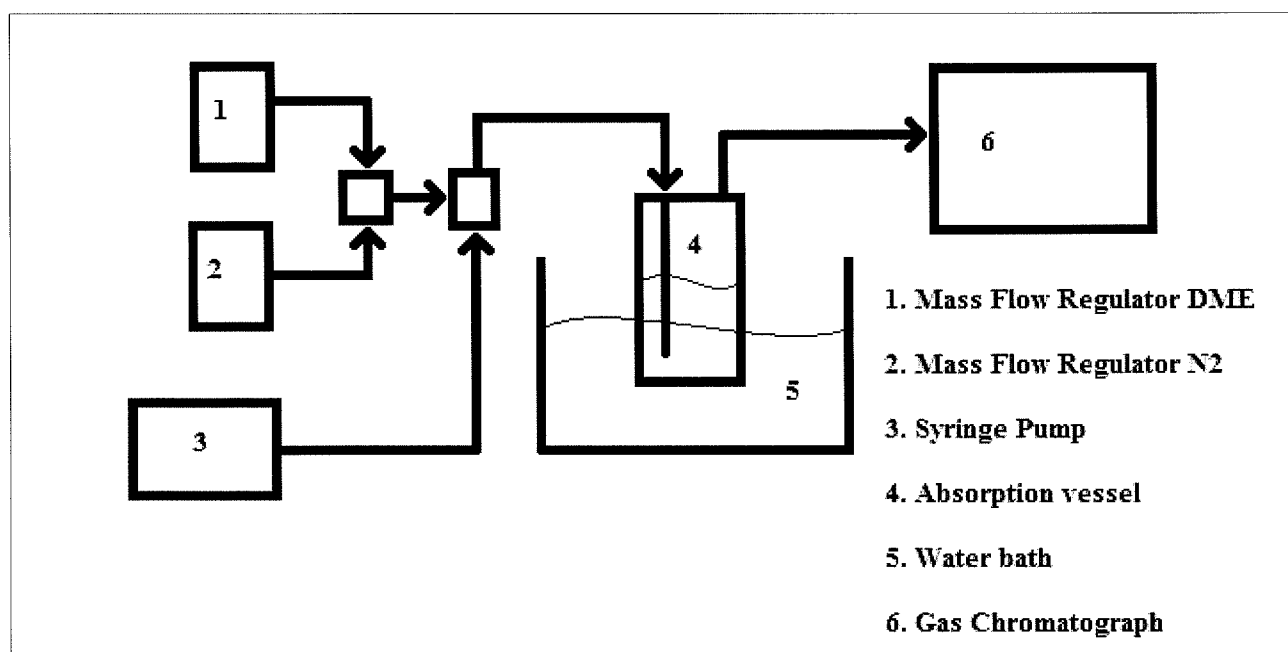


Figure 5. Schematic of the experimental setup

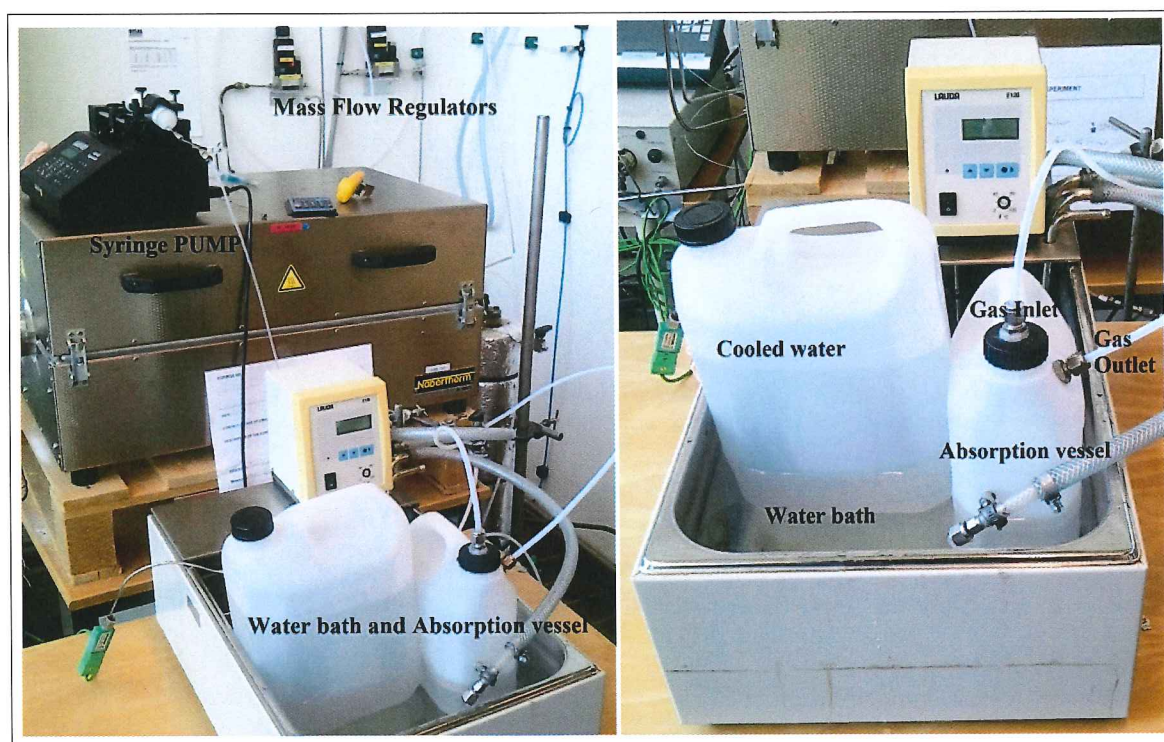


Figure 6. Pictures of the experimental equipment

Three temperatures and three compositions were investigated as displayed in Table 7 and Table 8.

Table 7 Temperatures used in the experiments.

Temperature [°C]	15	20	25
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Table 8. Compositions used in the experiments

Composition	DME	DME+MeOH	DME+MeOH+FA+H ₂ O
-------------	-----	----------	------------------------------

For each temperature and composition four runs were made where two went on until equilibrium was reached and two were shorter runs made to get more accurate result during the initial part of the runs. To get a good resolution one long and one short run was made with the chromatograph started right at the start of the runs and for the remaining runs it was started after one minute, except for the first experiments where it was started 30 seconds after the start of the runs. This meant that for each temperature and composition a data point was obtained every minute. As previously stated, the study was centred on DME and the rest of the compounds were merely added to investigate their effect on the absorbability of DME in water.

3.5.2 Interpretation of results

The data points were converted into moles of DME by the use of the ideal gas law and the calibration using a flow meter. The data points were then plotted and where there were double data points, since an additional shorter run was made for each composition and temperature, an average was used. 6th degree Polynomial trend lines were introduced and the equations of these trend lines were integrated using the trapezoid method. The amount of DME in the inlet gas (calibrated beforehand) was integrated and compared with the experimental integral and the difference between the two was seen as the amount of DME absorbed. This value was divided by an average of the amount of water used in the four runs regarding the specific temperature and compositions and the partial pressure of DME in the inlet gas (see Equation 9) creating a value comparable with the literature data and the theoretically calculated results.

$$\frac{\text{moles DME absorbed}}{\text{average volume water} \times \text{Partial pressure of DME in gas}} \quad (9)$$

3.6 Advanced simulation of single unit

A more realistic simulation was made to get more reliable results on which to base savings and cost estimations. Three thermodynamic models were tried but ultimately, the PSRK model was used for most of the simulation. The other two models were the Maurer model and the Wilson model. The components used are shown in Table 9.

Table 9. Molar composition of the gas stream going to the ECS

Component	Molar%
Dimethyl ether	0.33
Methanol	0.11
Formaldehyde	0.02
Nitrogen	89.27
Oxygen	5.29
Carbon monoxide	1.46
Carbon dioxide	0
Water	3.52

FA was omitted since the PSRK could not estimate interactions with the compound, which was noted in the basic simulations (See section 4.1.4). The other models used were the Maurer model and the Wilson model. The Maurer model could not handle DME and the Wilson model could not properly estimate the temperature when formaldehyde was absorbed but they both showed what had been hinted in the experimental part namely that most of the FA in the gas should be absorbed thus omitting it from the simulation would give reasonable results. To make the results more robust, DME was omitted, FA was introduced and the Maurer model was used to investigate how it estimated the absorbability of FA in the new unit.

The absorption unit was modelled as a tower+ unit with two inlet streams and two product streams. The total flow of the inlet gas stream was 635.87kmol/h and the inlet liquid stream was 57kmol/h, to account for possible condensation of water in the absorber. 2-6 stages were investigated and a stage efficiency of 70% was used based on [22]. Based on the investigations and the notion that the absorber could not be too big, 3 stages were chosen.

As mentioned above in section 1, the temperature development in the Emission Control System may cause problems thus making a decrease of hydrocarbons going to the ECS interesting. To simulate how much less heat would be generated in the ECS an isothermal Gibbs reactor unit was used in CHEMCAD. The Gibbs reactor unit in CHEMCAD calculates compositions and heat generated as the Gibbs free energy of an input stream is minimised. To get more robust results, in the case where the Maurer model was used, DME was added to the gas stream going from the absorber to the Gibbs reactor (ECS). The amount of DME added was the amount that was in the gas stream as estimated with the PSRK model. Notably a heater that increased the temperature of the gas stream to 200°C before the reactor was included. This unit is already present in the Formox-process and was thus neglected in the cost evaluations.

To simulate the temperature in the ECS without the new absorption unit the inlet gas stream was

simply inserted into a Gibbs reactor (after being heated). The simulation flow sheets are given in Figure 7 and Figure 8.

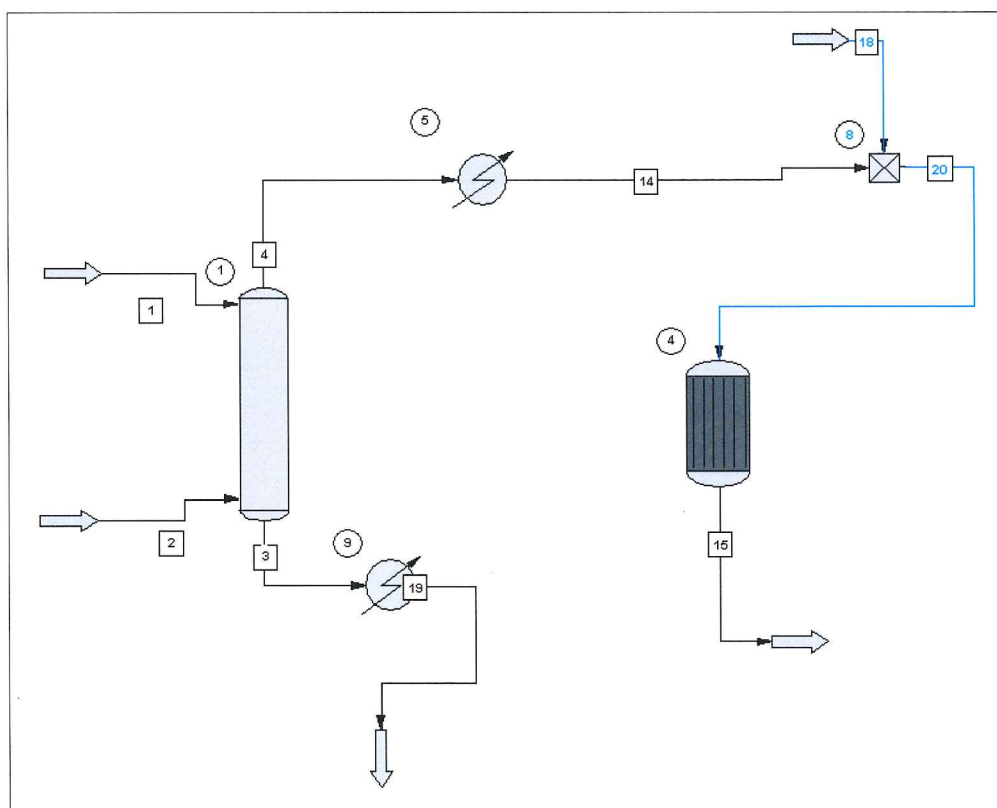


Figure 7. Simulation flow sheet of the absorber connected to the ECS

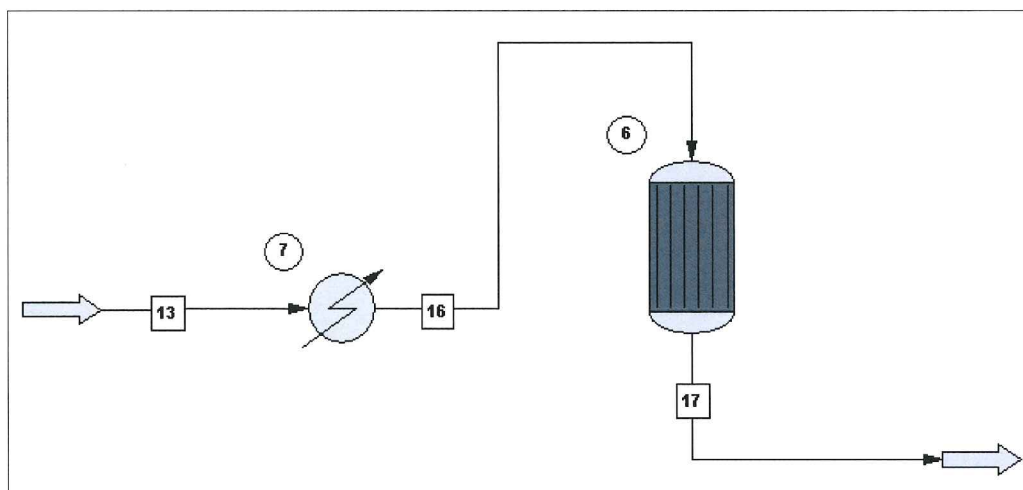


Figure 8. Simulation flow sheet of the ECS

3.7 Design and cost estimation

The sizing of the absorption unit simulated was done with the built in function in CHEMCAD. It was slightly modified to get more even dimensions. A basic design of the absorber was made based on this sizing, guide lines in [23] and some advice from some of Formox's process engineers [24]. The design is of an absorption unit standing freely. Another way of designing would be to put the new unit on top of the existing absorber which might lower the cost and not take as much room. To get more robust results the more expensive design was used. The design can be seen in Appendix 2.

3.7.1 Investment estimation

To get reliable information of what Formox would need to charge for the new absorber in a plant a simple estimation of the investment cost of the absorber was suggested by [25]. It was based on what Formox usually charge for the components in the absorber including a profit. Instead of following textbooks or finding prices from vendors, getting estimation from Formox itself was deemed more useful for the company. The basic estimation was deemed sufficiently accurate for this study.

3.7.2 Savings estimation

To be able to evaluate the economic feasibility of a new absorber the increase in yield had to be calculated. With systems not including FA this would preferably be made in a flow sheeting program such as CHEMCAD. In this thesis however, the difficult simulation of FA made it unwise to build a small process in CHEMCAD. Instead, mole balances for DME, MeOH and FA were made for simplified processes, one with the new absorber and one without. In Figure 9 the process flow sheet for the MeOH balance with the new absorber is shown. In appendix 3 all three flow sheets are shown along with descriptions in tables.

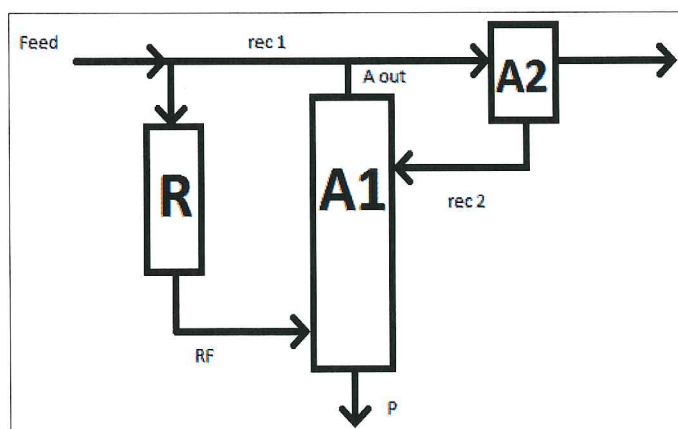


Figure 9. Flow sheet of the process with the new absorber, MeOH balance

The flow sheets differ from one another depending on what component is regarded. As for MeOH, the whole balance is based on a typical MeOH feed of a type of Formox plant. Known reaction yields for MeOH in the reactor (92.3% MeOH to FA, 1.8% MeOH to DME and 0.4% MeOH to CO) was used along with absorption degrees of MeOH in the existing absorber, calculated from customer data, and for the new absorber, calculated from CHEMCAD results. For DME, a production term from the reactor was used as a basis for the balance. This term was calculated from the MeOH feed by using the reaction yields mentioned. The absorption degrees for DME were obtained in the same way as for MeOH but the reaction yields (90% DME to FA and 9% DME to CO) was suggested by two of Formox's R&D associates. The FA balance was made in the same way as the DME balance; reaction yields (4% FA to CO, the rest not reacted) from Formox's R&D associates, absorption degrees from data and CHEMCAD.

The balances without a new absorber were simpler since they did not include a second recycle stream. In Figure 10 the flow sheet for the MeOH balance is shown. In Appendix 3, all three process flow sheets are shown along with descriptions.

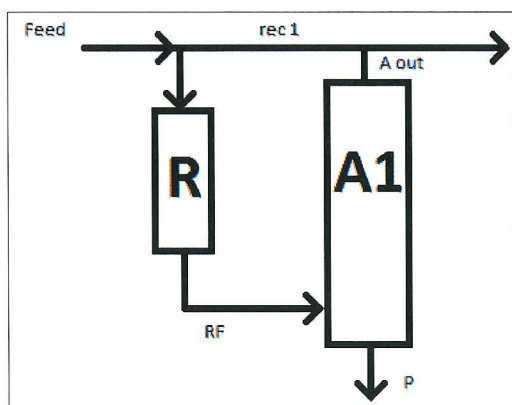


Figure 10 . Flow sheet of the process without the new absorber, MeOH balance

With the streams known the two processes were compared by adjusting the methanol feed in the new absorber-process to give the same amount of formaldehyde in the product stream as what was obtained in the process without a new absorber. The difference between the needed methanol feed for the processes is the basis for the savings the addition of a new absorber can give. With less hydrocarbons going to the ECS, the heat created in that reactor is less than the case without a new absorber. While this would be beneficial for plants where the ECS is the limit for operation of the total plant, the decrease in heat production, which means less steam production, may be expensive. The decreased steam production serves as another cost, apart from the investment cost, of the new absorber. The amount of steam “lost” was calculated from the difference in heat production in the Gibbs reactor in CHEMCAD. The heat was compared with the vaporisation enthalpy (2356 kJ/kg) for water in the ECS’s boiler [26]. By dividing the heat loss (kJ/h) with the enthalpy (kJ/kg) an amount of steam lost per hour was obtained.

3.7.3 Economics

Two economic evaluations were made, one with 100% absorption of the formaldehyde in the new absorber and one with an absorption degree from CHEMCAD as mentioned above in section 3.6. In the evaluation the MeOH savings, the steam loss and the investment cost were used as a basis. The price of MeOH used was 340 €/ton and the price of steam used was 20 €/ton. These prices are common in the European market according to [26]. A value of 9.27 SEK/€ was used. A possible cost that was not included was that of cooling the process water to 15°C. The temperature of the process water varies between plants but in this study the temperature was fixed at 15°C.

The profitability of the new absorber was evaluated in three ways; Pay Back Period, Net Future Worth and Net Present Worth.

The Pay Back Period, or PBP, describes how long it takes to pay for the investment with the savings it achieved and is calculated as follows:

$$\frac{\text{investment cost}}{\frac{\text{savings}}{\text{year}}} = PBP [\text{years}] \quad (10)$$

The Net Future Worth, or NFW, is the cumulated profit of the investment over the life time of the new equipment. It is calculated as in equation 11 below.

$$NFW = \sum_{i=0}^{End\ of\ life\ time} (savings\ year_i - cost\ year_i) \quad (11)$$

The Net Present Worth, or NPW, converts the net future worth to depend on the value of money. An interest rate is introduced (in this study 0.05) and the profit in a year is converted into what that money would be worth today (or start of the project) [27].

$$NPW = \sum_{i=0}^{End\ of\ life\ time} \left(\frac{profit\ year_i}{(1 + interest\ rate)^{year_i}} \right) \quad (12)$$

3.8 Sensitivity analysis

To test the robustness of the investment a sensitivity analysis was made. Four parameters were varied as can be seen in Table 10.

Table 10. The parameters and values used in the sensitivity analysis

Methanol price SEK/ton	Steam price SEK/ton	Investment cost SEK	Temperature of process water °C
-50%	-50%	-50%	10
-25%	-25%	-25%	12,5
3153	185	500000	15
25%	25%	25%	17,5
50%	50%	50%	20

By varying the temperature of the process water, the degree of absorption was varied. The sensitivity analysis was made for both the case with 100% absorption of formaldehyde and the case with formaldehyde absorption based on the Maurer model. PBP, NFW and NPW were used in the analysis.

4 RESULTS AND DISCUSSION

4.1 Degree of absorption results

4.1.1 Henry's law

As stated above in Theoretical calculations, Henry's law calculations were carried out for the DME-water and MeOH-water systems.

In Table 11 and Table 12 the results for these systems are displayed.

Table 11. Results from Henry's law calculations and literature based calculations for DME in water

Temperature	unit	0°C	10°C	20°C	25°C	30°C
Henry's Law	kmol/h	0.009	0.006	0.005	0.004	0.003
Henry's Law	mol/m ³ Pa	0.022	0.016	0.011	0.010	0.009
Literature data	kmol/h	0.011	0.007	0.004	0.004	0.003
Literature data	mol/m ³ Pa	0.027	0.017	0.011	0.010	0.008

Table 12. Results from Henry's law calculations for MeOH in water

Temperature	unit	15°C	20°C	25°C
Henry's Law	kmol/h	0.52	0.38	0.28
Henry's Law	mol/m ³ Pa	3.98	2.92	2.17

The values are in two forms; mole per cubic meter water Pascal and kmol per hour for a unit with a 44kmol/h flow of water, and were calculated with the gas compositions given in Table 9. The flow of water was used to make the values comparable to the values from the basic simulations in which a water flow of 44kmol of water per hour was used.

For the DME-water system the Henry constants were calculated by the uses of the vapour pressures. The vapour pressures given in [19] were used with the constant from [7]. The vapour pressures were, as mentioned earlier, similar to pressures found in other studies. The vapour pressure data from [19], [21] and [20] can be seen in Appendix 4.

4.1.2 Literature data

The DME-water system was the only system for which calculations based on literature data were carried out. This was because of the scarcity of such data for the other compounds at the temperatures of interest and the focus on DME in the thesis.

In Table 11 the results are given and they are similar to the result from the calculations with Henry's law. This was found very interesting since the Henry coefficient for DME in water given by [7] is based on a completely different study than the literature data thus validating the results to some extent. A plot of the literature data can be seen in Appendix 5.

4.1.3 Experimental data

The experimental data obtained from the Gas chromatograph were in the form as shown in the figures in Appendix 6. Chromatograms from experiments along with more precise data shown in the table in the same appendix. The peaks represent different components and the respective area relates to the amount (though differently for each compound). By comparing the first and the second figure one can see that the amount of DME increases with time. The third figure show a run made without water but with inert glass pearls (used for calibration as described above). In the fourth figure a small MeOH peak is visible and by comparing with the fifth figure, one sees that

MeOH is easily absorbed since the fifth figure represent the system some 30 min after the start, well after equilibrium was reached for DME. In the last figure FA was included, but it is not visible in the chromatogram, indicating that all of it was absorbed in the vessel.

As stated above in section 3.5.1, the data points for each temperature and composition were plotted and 6th degree polynomial trend lines were added. In Figure 11 one of these plots is shown and the rest are given in Appendix 8. The plots show the initial concentration as that of the first data point. In reality the initial concentration in the absorption vessel is zero but since the first measurements were made just a few seconds after the start of the runs, the difference in amount absorbed was seen as negligible. The plots in Appendix 8. Plots of experimental results differ in time scales because longer runs were needed to reach equilibrium at the lower temperatures.

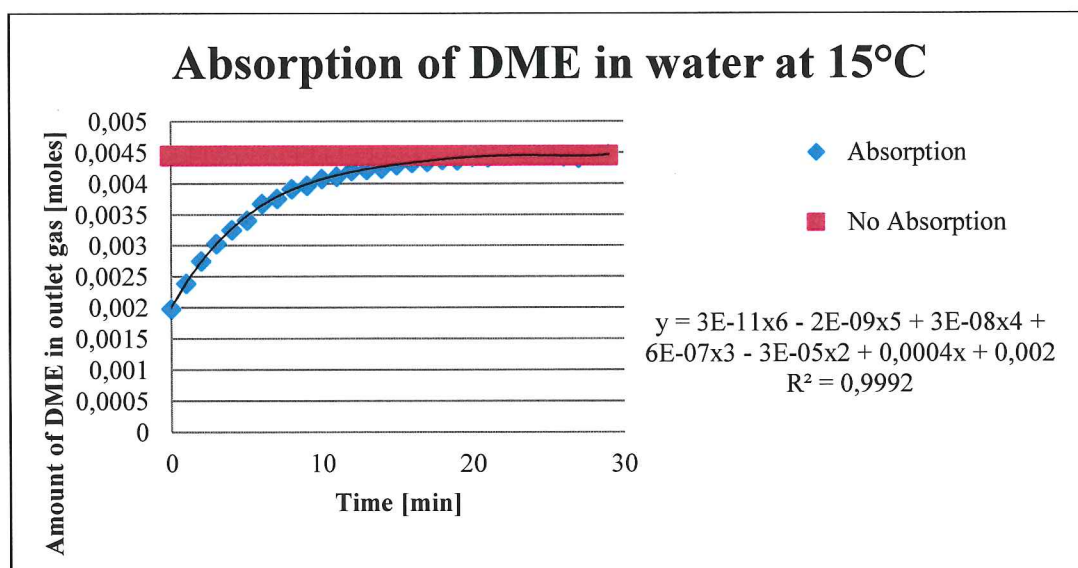


Figure 11. Plot of experimental data along with an equilibrium line and a polynomial trend line

The results from the absorption of DME in water for all temperatures and compositions are displayed in Table 13.

Table 13. Experimental results of the absorbability of DME in water

Composition	unit	Temperature		
		15°C	20°C	25°C
DME	kmol/h	0.005	0.004	0.003
DME	mol/m ³ Pa	0.013	0.010	0.008
DME+MeOH	kmol/h	0.004	0.004	0.003
DME+MeOH	mol/m ³ Pa	0.010	0.010	0.009
DME+MeOH+FA	kmol/h	0.005	0.004	0.003
DME+MeOH+FA	mol/m ³ Pa	0.013	0.010	0.007

By comparing the experimental results with the results from the theoretical calculations and the literature data (given in Table 11 and Table 12) one sees that they are indeed quite alike. This may serve as a confirmation of the previous calculations. It is clear from this data that the absorbability of DME is very poor, at least from a recovery perspective. In the gas stream, mentioned in section 1, 2.09 kmol/h of DME/h was present. In Table 14 the absorption degrees at 20°C and a water flow of 59 kmol/h for the literature based calculations, theoretical calculations and the experimental results are shown.

Table 14. Absorption degrees of DME for the literature based calculations, theoretical calculations and the experimental results at 20°C

Literature based calculations	0.21%
Theoretical calculations	0.21%
Experimental results	0.18%

Just by looking at the experimental results one sees that the temperature is much more influential than the addition of other components. To confirm this, a simple ANOVA table was constructed in Microsoft Excel's statistical add-in which is displayed in Table 15. The data used to make the ANOVA table was the data in table 13 which had the unit moles/m³Pa and α was 0.05.

Table 15. Anova-table for the experimental results

Anova: Two-Factor Without Replication						
<i>SUMMARY</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
DME	3	0,030	0,010	5,81E-06		
DME+MeOH	3	0,029	0,010	1,02E-06		
DME+MeOH+FA	3	0,030	0,010	7,77E-06		
15°C	3	0,036	0,012	1,95E-06		
20°C	3	0,030	0,010	5,28E-08		
25°C	3	0,024	0,008	4,98E-07		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Compositions	3,63E-07	2	1,82E-07	0,156	0,860	6,944
Temperatures	2,46E-05	2	1,23E-05	10,578	0,025	6,944
Error	4,64E-06	4	1,16E-06			
Total	2,96E-05	8				

From the ANOVA table it was clear that, statistically, the temperature was influential on the degree of absorption while the different compositions were not, even though the 15°C value for the MeOH-DME-water system deviated from the trend. This deviation most likely occurred because the temperatures in these experiments were not actually 15°C.

With the results from the experiments it was clear that the addition of methanol and formaldehyde did not increase the degree of absorption of DME in water, at least not in the concentrations studied.

4.1.4 Basic simulation data

As mentioned earlier, the basic simulations were made in order to get information on which thermodynamic model to use. The results from these simulations can be viewed in Table 16 below. The Maurer model simulations at 0 and 10°C did not converge, thus the blank spaces in Table 16.

Table 16. Results from the Basic simulations with four different thermodynamic models and experimental results for comparison

Model	Component	unit	Temperature				
			0°C	10°C	15°C	20°C	25°C
Wilson	DME	kmoles/h	0.012	0.011	0.011	0.011	0.011
	FA	kmoles/h	0.13	0.13	0.13	0.13	0.13
	MeOH	kmoles/h	0.277	0.271	0.274	0.274	0.273
PSRK	DME	kmoles/h	0.005	0.005	0.005	0.005	0.005
	FA	kmoles/h	0.003	0.003	0.003	0.003	0.003
	MeOH	kmoles/h	0.183	0.177	0.175	0.172	0.170
UNIFAC	DME	kmoles/h	0.007	0.007	0.007	0.007	0.007
	FA	kmoles/h	0.004	0.004	0.003	0.003	0.003
	MeOH	kmoles/h	0.184	0.178	0.176	0.173	0.170
Maurer	DME	kmoles/h	-	-	0.075	0.075	0.075
	FA	kmoles/h	-	-	0.13	0.13	0.13
	MeOH	kmoles/h	-	-	0.222	0.221	0.220
Experimental results	DME	kmoles/h	-	-	0.005	0.004	0.003

From these simulations it was clear that the UNIFAC and the PSRK models estimated the absorbability of FA very poorly. With such absorbability FA could hardly be absorbed the way it is done in the Formox-process. The Maurer model gave a much higher absorbability of DME than the other models while the Wilson model gave slightly higher absorbability of DME than the PSRK and the UNIFAC models but absorbability of FA similar to that of the Maurer model. After comparing these results with the experimental results, The PSRK model was seen as the most accurate model regarding DME. The Wilson model showed a high temperature increase as FA was absorbed which was deemed unreliable and there for the PSRK model was used, without FA present, since accuracy on the absorbability of DME was considered more important than that of FA in the thesis.

By comparing the results in Table 12 with the results in Table 16 one sees that the values for methanol in the simulations are about the same as for the theoretical calculations at 25°C.

As for the temperature dependencies, CHEMCAD does not seem to estimate them to be of great importance for neither DME nor MeOH. In the Henry's law calculations, given in Table 11 and Table 12, the temperature dependencies for both components were large.

4.2 Results from advanced simulations

4.2.1 Absorber

As mentioned above in section 3.6 three stages were used. Four stages would have been better in a recovery point of view but it was deemed to be too large, thus three stages were used. Plots of the absorption of DME and MeOH are shown in Appendix 7.

The more realistic simulations were made for the temperatures 10°C, 12.5°C, 15°C, 17.5°C and 20°C. 15°C was the main case while the data from the other simulations were used in the sensitivity analysis. The simulations were made in two versions, one with the PSRK model and FA omitted and

one with the Maurer model and DME omitted. In Table 17 the amount of DME and MeOH recovered for the PSRK case (or Full FA absorption case) is shown and in Table 18 the amounts of FA and MeOH recovered for the Maurer case are shown. Included are also how much of DME and MeOH that was recovered (in mole percentages), which were used in the savings estimations.

Table 17. Results from the advanced simulations with the PSRK model and FA omitted

Component	unit	Temperature of process water				
		10.0°C	12.5°C	15.0°C	17.5°C	20.0°C
DME	kmol/h	0.0049	0.0049	0.0048	0.0048	0.0048
DME	Mole%	0.233	0.232	0.231	0.231	0.230
MeOH	kmol/h	0.171	0.170	0.170	0.169	0.168
MeOH	Mole%	25.07	24.99	24.91	24.83	24.75
H ₂ O	kmol/h	59.132	58.965	58.798	58.630	58.462

Table 18. Results from the advanced simulations with the Maurer model and DME omitted

Component	unit	Temperature of process water				
		10.0°C	12.5°C	15.0°C	17.5°C	20.0°C
MeOH	kmol/h	0.157	0.156	0.156	0.155	0.155
MeOH	Mole%	23.03	22.96	22.88	22.80	22.72
FA	kmol/h	0.114	0.114	0.114	0.114	0.114
FA	Mole%	88.01	87.93	87.85	87.77	87.69

4.2.2 ECS-model

For the case with full FA absorption (PSRK model) the stream from the absorber was heated and then inserted into the Gibbs reactor. For the Maurer case, DME was added after the absorber to give more accurate results in the Gibbs reactor. The temperature and the heat generated for the two cases at the given temperatures are shown in Table 19 and Table 20. In Table 21 the temperature and heat generated for the present process (without the new absorber) are shown.

It is not visible in Table 19 but the temperature in the ECS actually decreases slightly, while the heat generated on the other hand increases, as the temperature of the process water increases. In the simulations with the Maurer model the system did not behave in this way, as can be seen in Table 20. Why the system behaves like this is hard to explain, but it could just be a miscalculation in CHEMCAD. The behaviour was not further investigated.

Here it can be seen that by introducing the extra absorption unit the temperature rise over the ECS reactor will decrease by some 8-9°C.

Table 19. Results from the simulations of the ECS with the PSRK model and Full FA absorption assumed

	10.0°C	12.5°C	15.0°C	17.5°C	20.0°C	
Heat generated in ECS	5749	5749	5750	5750	5751	MJ/h
Temperature in ECS	493	493	493	493	493	°C

Table 20. Results from the simulations of the ECS with the Maurer model and DME added after the absorber

	10.0°C	12.5°C	15.0°C	17.5°C	20.0°C	
Heat generated in ECS	5767	5767	5767	5768	5768	MJ/h
Temperature in ECS	494	494	494	494	494	°C

Table 21. Results from simulation of the ECS without a new absorber (same values with both the PSRK and Maurer models)

Heat generated in ECS	5938	MJ/h
Temperature in ECS	502	°C

4.3 Results from the savings estimation

The overall yield was calculating by dividing the moles of FA produced with the feed of moles MeOH. The amounts of moles were calculated as described in section 3.7.2.

The yields for the full FA absorption case and for the Maurer based case are shown in Table 22.

Table 22. Estimated yields for the present process, the Full FA Absorption case and the Maurer based case

Present process	Full FA Abs	Maurer based
93.91%	93.99%	93.98%

4.4 Results from the economic evaluation

4.4.1 Investment

The estimated cost of the components in the absorber is displayed in Table 23. The installation cost is included in the price. The cost estimation is for a self-standing absorber without stands, ladders and piping to the process.

Table 23. The estimated investment cost of the new absorption unit

Cost absorber components, Investment and installation SEK	
Gables	10000
Mantle	50000
Support rings etc.	50000
Trays	120000
Sum Components	320000
Risk	80000
Profit	100000
Total	500000±20000

4.4.2 Economics

For the case based on the Maurer model, as mentioned above, the MeOH savings amounted to 5.62 kg /h which translates to 17.72 SEK/h and the steam loss amounted 70 kg/h which translates to 13.46 SEK/h. For the case with 100% FA absorption in the new absorber the MeOH savings amounted to 6.35 kg/h, 20.01 SEK/h, and the steam loss was 80 kg/h, 14.84 SEK/h.

The process was assumed to operate 333 days per year which equals 7992 hours per year. The Pay Back Period, Net Future Worth and Net Present Worth for both of the cases are presented in Table 24 and in Figure 12 and Figure 13 the NFW and NPW over the life time for both cases are shown. The NFW and NPW were calculated for a 30 year life time.

Table 24. Pay Back Period, Net Future Worth and Net Present Worth for the two cases

	PBP years	NFW MSEK	NPW MSEK
Full FA abs	12.1	0.742	0.136
Maurer	14.7	0.523	0.024

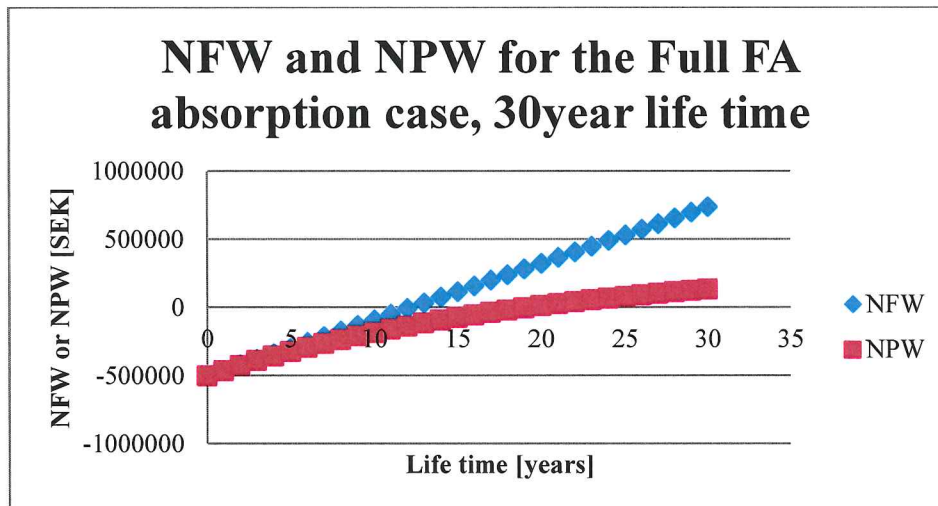


Figure 12. Graph of how the NFW and the NPW changes over the life time for the Full FA absorption case (interest rate of 0.05)

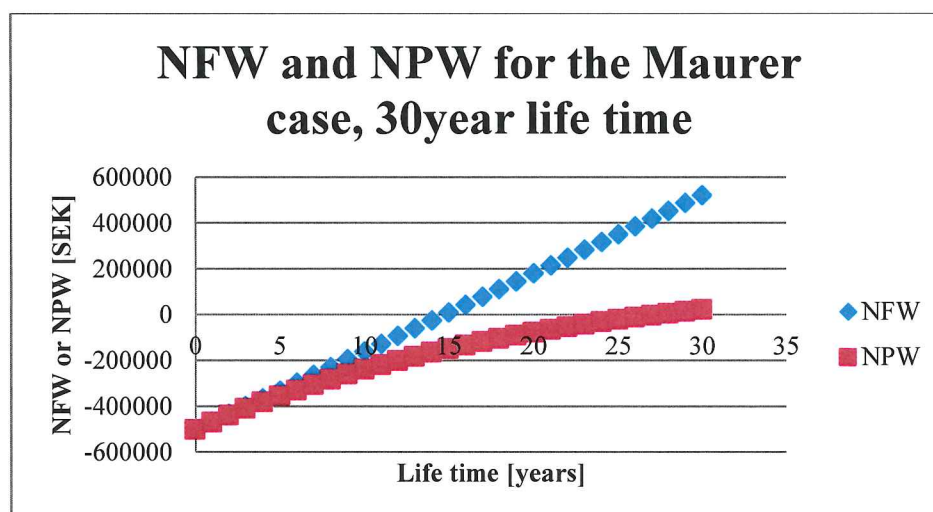


Figure 13 Graph of how the NFW and the NPW changes over the life time for the Maurer based case (interest rate of 0.05)

As expected the case with full formaldehyde absorption is more profitable but neither case shows good profitability, the NPW only turning positive after 19 years of operation for the full absorption case and 28 years for the Maurer based case.

4.5 Sensitivity analysis

As described in method the sensitivity analysis used four parameters to vary and PBP, NFW and NPW as results. In Appendix 9. Sensitivity analysis plots the dependencies of PBP, NFW and NPW on the parameters are shown. The first three are for the Full FA absorption case. Since the methanol price affects the savings it has a positive slope instead of a negative which the other parameters do because they affect costs. In Figure 14 the NFW of the Full FA absorption case is shown. The temperature dependency did not vary in the same way as the other parameters for the Maurer based case but.

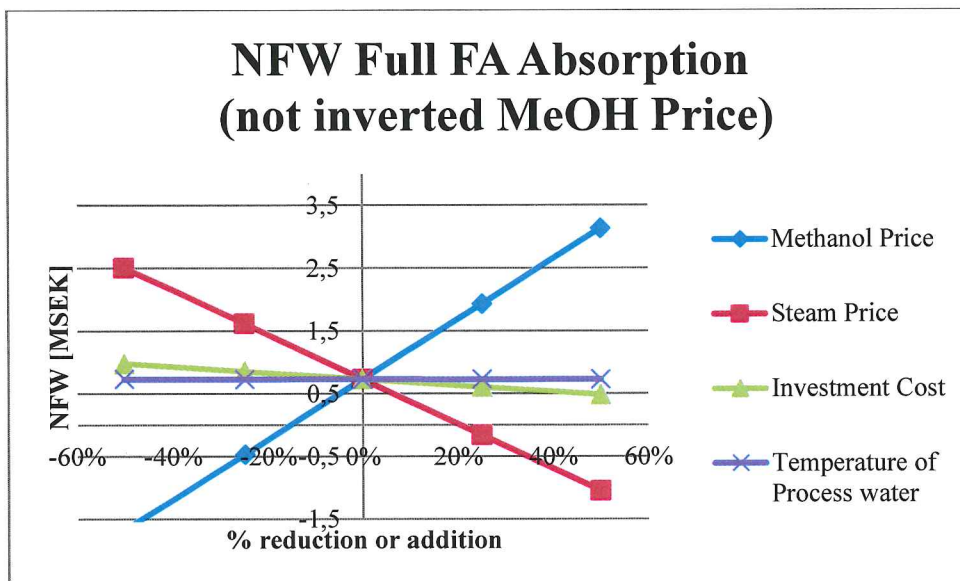


Figure 14. Sensitivity analysis of the Net Future Worth without the methanol price inverted

Some values are not included in the PBP-plots. This is because the missing values were negative, meaning a case which was not profitable at all.

What can be deduced from the figures is that the parameter which the results are most dependent on is the methanol price. The steam price was the second most dependent and then came the investment cost. The temperature dependency is low as seen in section 4.2.1. It is likely that CHEMCAD cannot estimate the temperature dependencies accurately.

5 CONCLUSIONS

5.1 Absorbability of dimethyl ether

The results, both theoretical and experimental, show modest absorbability of DME in water. This was expected, but not qualitatively known at Formox. From the results it was found that the modification of Henry's law, as described in the section about Henry's law, provided results very similar to those found in the literature. This validates the procedure making it interesting for future researchers who face difficulties in finding values for the Van't Hoff equation.

The experimental results were somewhat different from the literature and theoretical results though similar enough to indicate that the literature data are reliable. The experimental procedure was very simple and the equipment used was not design for these types of experiments originally. Because of this, many sources of error existed and they may account for the differences between the experimental and the literature results. One possible source of error is the mass flow regulators which were very sensitive to pressure changes, another the fact that the temperature inside the absorption vessel was not monitored.

In the literature it was suggested that MeOH could enhance the absorbability of DME but this was not proven in the experiments. The experimental results showed that the additional components did not alter the absorbability but this may be because of the low concentrations of the components. Although the gas stream going to the ECS holds these low concentrations, it might be of interest to Formox how they affect DME absorbability at higher concentrations. Therefore, it might be something to investigate further in the future.

As the absorbability of DME was found to be low, adjustment of the catalyst loading profile, to obtain more DME and less CO than before, is not advisable since the DME cannot be significantly recovered in a new absorption unit.

5.2 Simulation

Firstly, the simulations showed that the components investigated presented difficulties for the thermodynamic models used in CHEMCAD. No model could estimate the system with all components present accurately enough, much because of the presence of FA.

Something noteworthy was that CHEMCAD could not estimate temperature dependencies very well for neither DME nor MeOH. It was clear from theoretical, literature and experimental data that the temperature was influential on the absorbability.

The simulations of the ECS showed that the heat generated could be lowered enough to account for some of the problems in plants where the ECS is a bottleneck by decreasing the temperature by some 8-9°C.

5.3 Economic evaluation

Even though the proposed absorber gave very modest recovery of DME, the unit could pay for itself because of the absorption of FA and MeOH, according to the CHEMCAD simulations. These savings were not extensive however and the sensitivity analysis showed that the profitability of the new absorber was not very robust since it was highly dependent on several parameters.

If MeOH and FA could be recovered to the extent shown in the simulations, it might be interesting to introduce some kind of recovery unit. This new unit could be additional stages in the existing absorber with the recycle stream taken out as a side stream before these stages. The economic feasibility of this would then depend on if the absorbability of MeOH and FA are good enough and that the additional stages (or new unit) are cheap enough to implement. In order to fully evaluate if

there could be any economically feasible recovery from the gas stream going to the ECS, the absorbability of MeOH and FA need to be thoroughly investigated, which it was not in this study. One could calculate the savings based on full MeOH absorption, but how useful such an investigation is depends on the actual maximum absorption of MeOH.

How the lowered generated heat in the ECS affects the profitability of the unit is different for every plant. In some cases the ECS poses such a problem that other units not found in most plants such as addition of air before the ECS must be included. In such cases the profitability of the new absorption unit may be larger than the present solutions would be. Therefore the new absorber can be suggested to these plants but should be investigated specifically for the plant in question before it is introduced since an 8-9°C temperature decrease may not be enough [2].

5.4 Summary

The conclusion of this thesis is that the introduction of a new absorption unit in the Formox-process is not economically feasible due to the poor savings and high investment cost it introduces. The absorption of DME in water is too low for an economic recovery of the component from the gas stream. More research is needed to evaluate if the recovery of MeOH and FA could be economically feasible.

6 ACKNOWLEDGEMENTS

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Some special thanks to **Robert** for doing a great job as supervisor and for the help with my stay in Perstorp, to **Christian** for all the help and for acting as supervisor when Robert was not available and to **the guys in the lab** for the help and the fun time working there.

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Appendix 1. Chart for choosing thermodynamic model

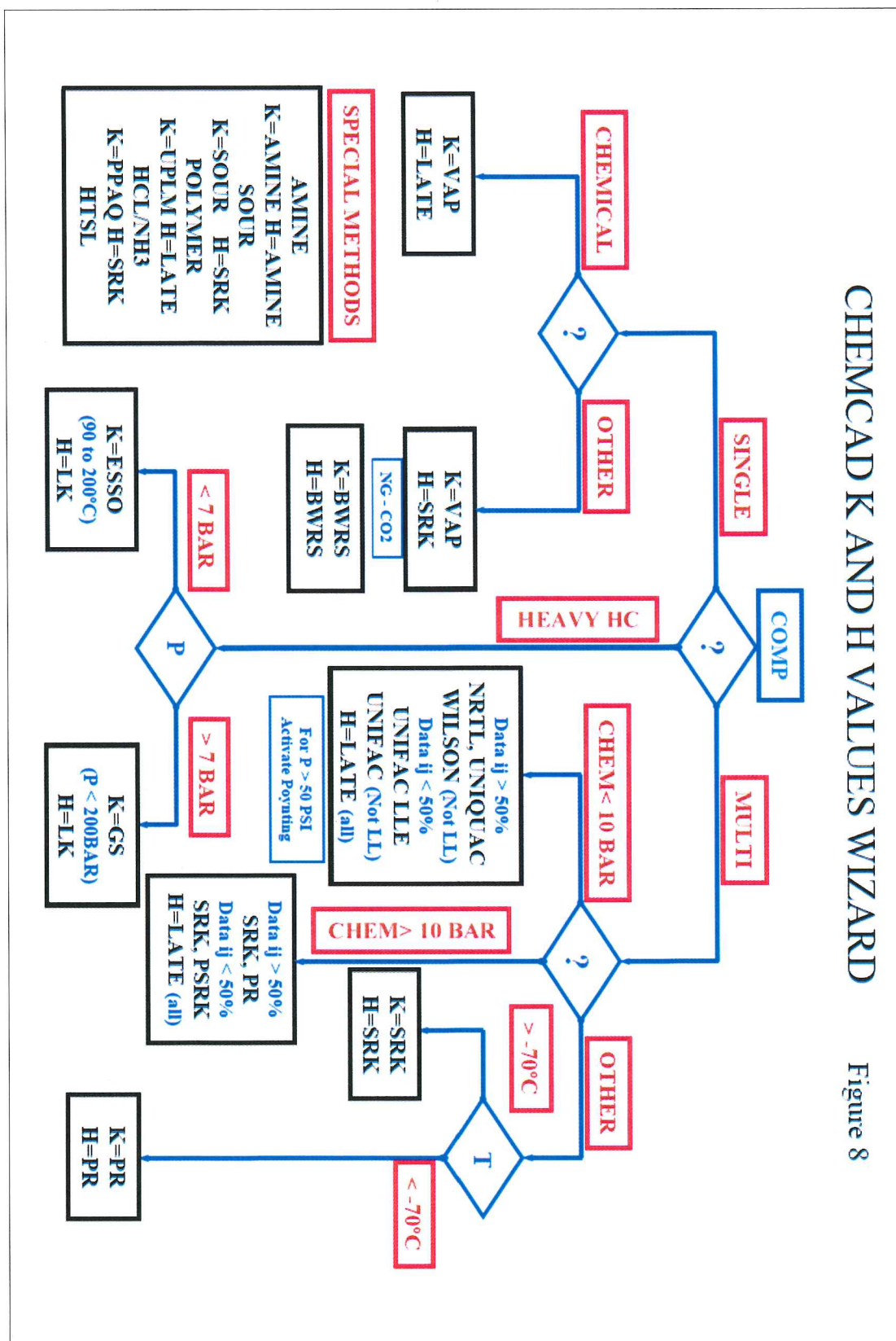
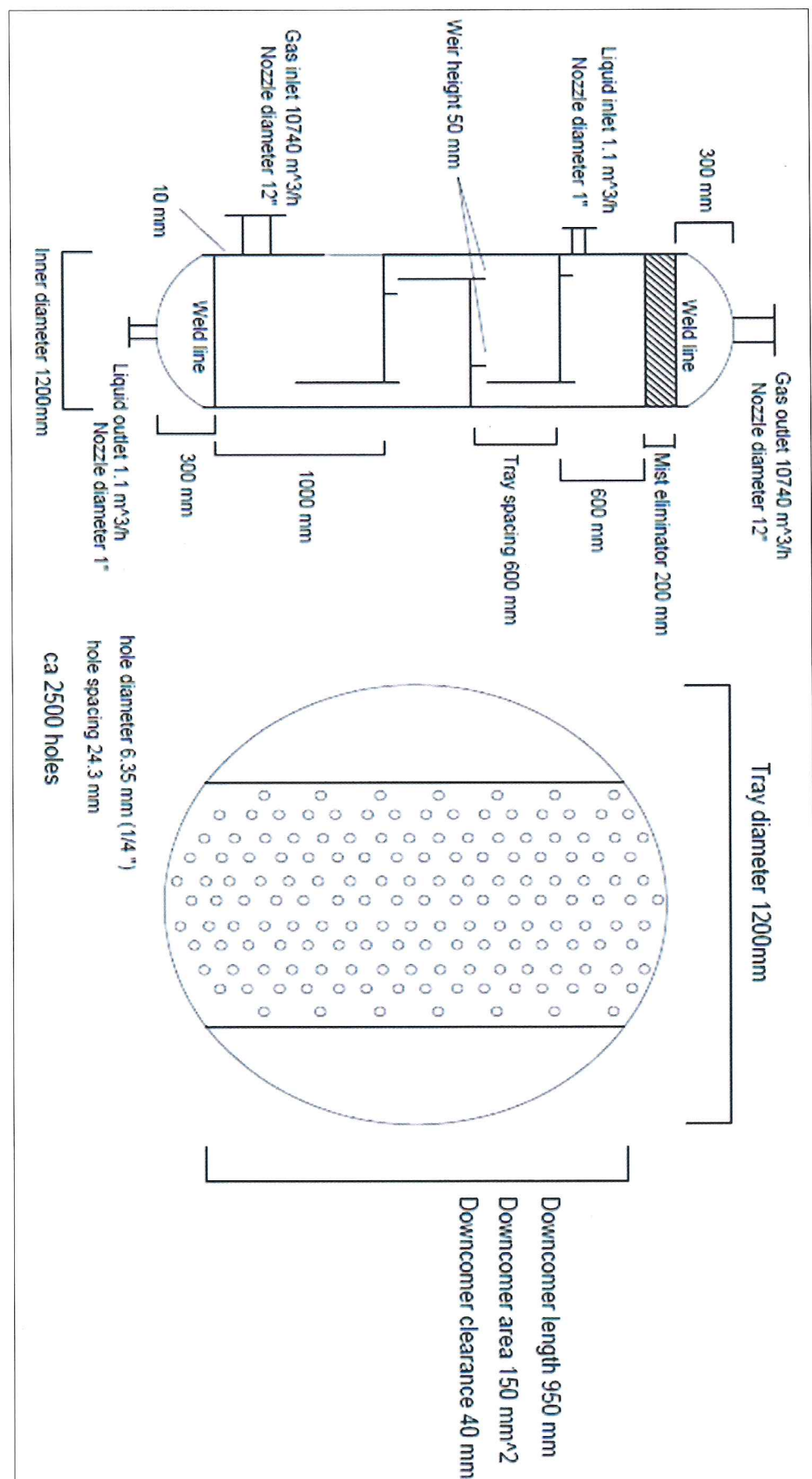


Chart for choosing a thermodynamic model for simulations [12]

Appendix 2. Basic sketch of the new absorption unit

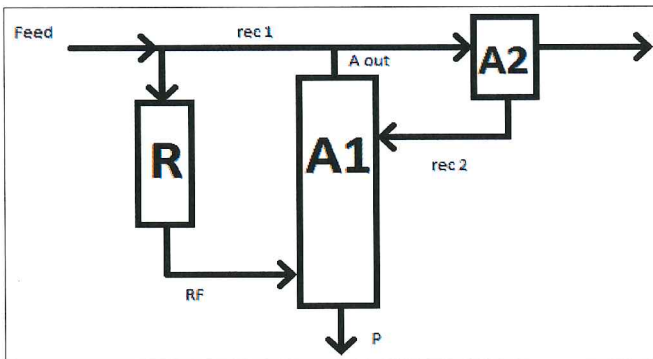


Basic sketch of the new absorber

Appendix 3. Explanations of the savings estimation

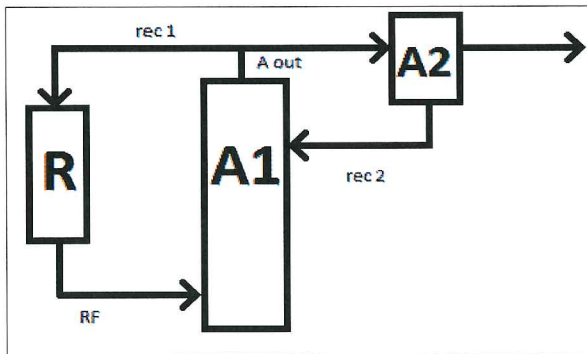
Explanations of streams shown below

Feed: Feed stream of MeOH
Prod: Production of DME or FA
rec 1: Recycle stream from Absorber 1
rec 2: Recycle stream from Absorber 2
P: Product stream from process
RF: Reactor outflow
Aout: Top outlet from Absorber 1



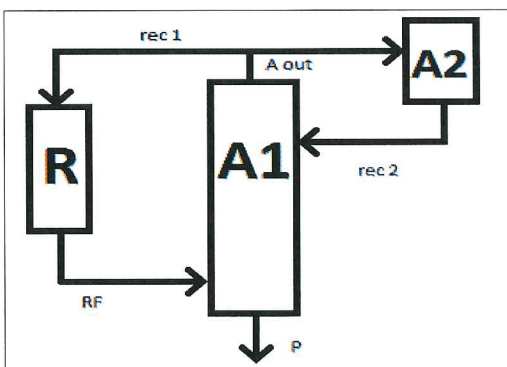
$RF = (Feed + rec1)(1 - x1 - x2 - x3)$
$Aout = (f + rec1)(1 - x1 - x2 - x3)(1 - x4) + rec2(1 - x4)$
$rec1 = Aout * 2/3$
$rec2 = Aout * 1/3 * x5$
$P = (f + rec1)(1 - x1 - x2 - x3)(x4) + rec2(x4)$
$x1 = \text{reaction degree MeOH to FA}$
$x2 = \text{reaction degree MeOH to DME}$
$x3 = \text{reaction degree MeOH to CO}$
$x4 = \text{absorption degree absorber 1}$
$x5 = \text{absorption degree absorber 2}$

MeOH balance with new absorber (A2) along with equations in the table



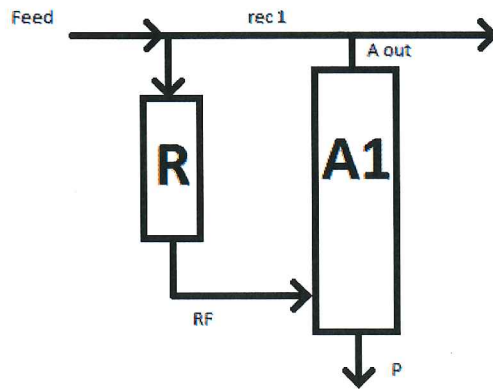
$RF = (Prod + rec1)(1 - x1 - x2)$
$Aout = (f + rec1)(1 - x1 - x2) + rec2$
$rec1 = Aout * 2/3$
$rec2 = Aout * 1/3 * x3$
$x1 = \text{reaction degree DME to FA}$
$x2 = \text{reaction degree DME to CO}$
$x3 = \text{absorption degree absorber 2}$

DME balance with new absorber (A2) along with equations in the table



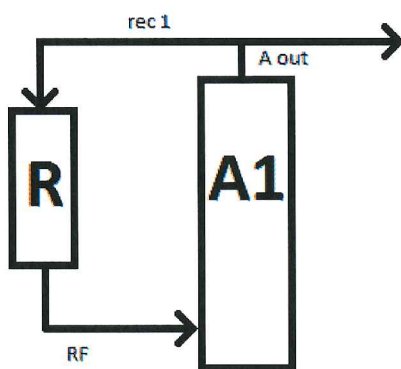
$RF = (Prod + rec1)(1 - x1)$
$Aout = (prod + rec1)(1 - x1)(1 - x2) + rec2(1 - x2)$
$rec1 = Aout * 2/3$
$rec2 = Aout * 1/3 * x3$
$P = (prod + rec1(1 - x1))(x2) + rec2(x2)$
$x1 = \text{reaction degree FA to CO}$
$x2 = \text{absorption degree absorber 1}$
$x3 = \text{absorption degree absorber 2}$

FA balance with new absorber (A2) along with equations in the table



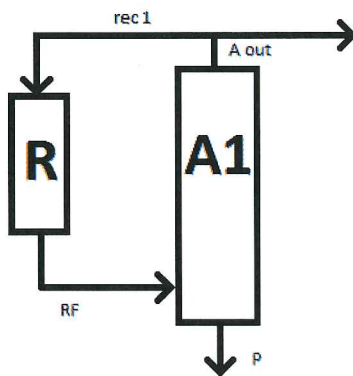
$RF = (Feed + rec1)(1 - x1 - x2 - x3)$
$Aout = (f + rec1)(1 - x1 - x2 - x3)(1 - x4)$
$rec1 = Aout * 2/3$
$P = (f + rec1)(1 - x1 - x2 - x3)(x4)$
$x1 = \text{reaction degree MeOH to FA}$
$x2 = \text{reaction degree MeOH to DME}$
$x3 = \text{reaction degree MeOH to CO}$
$x4 = \text{absorption degree absorber 1}$

MeOH balance without new absorber along with equations in the table



$RF = (Prod + rec1)(1 - x1 - x2)$
$Aout = (f + rec1)(1 - x1 - x2)$
$rec1 = Aout * 2/3$
$x1 = \text{reaction degree DME to FA}$
$x2 = \text{reaction degree DME to CO}$

DME balance without new absorber along with equations in the table



$RF = (Prod + rec1)(1 - x1)$
$Aout = (prod + rec1)(1 - x1)(1 - x2)$
$rec1 = Aout * 2/3$
$x1 = \text{reaction degree FA to CO}$
$x2 = \text{absorption degree absorber 1}$

FA balance without new absorber along with equations in the table

Appendix 4. Vapour pressure data of DME from three sources

Vapour pressure data at different temperatures from [19] (VP of 298.15 K was interpolated)

T [11]	P kPa
273,13	266,8
283,02	372,3
293,08	508,9
297,07	573
298,15	591,22
299,08	606,9
303,08	680,2
313,06	889,5

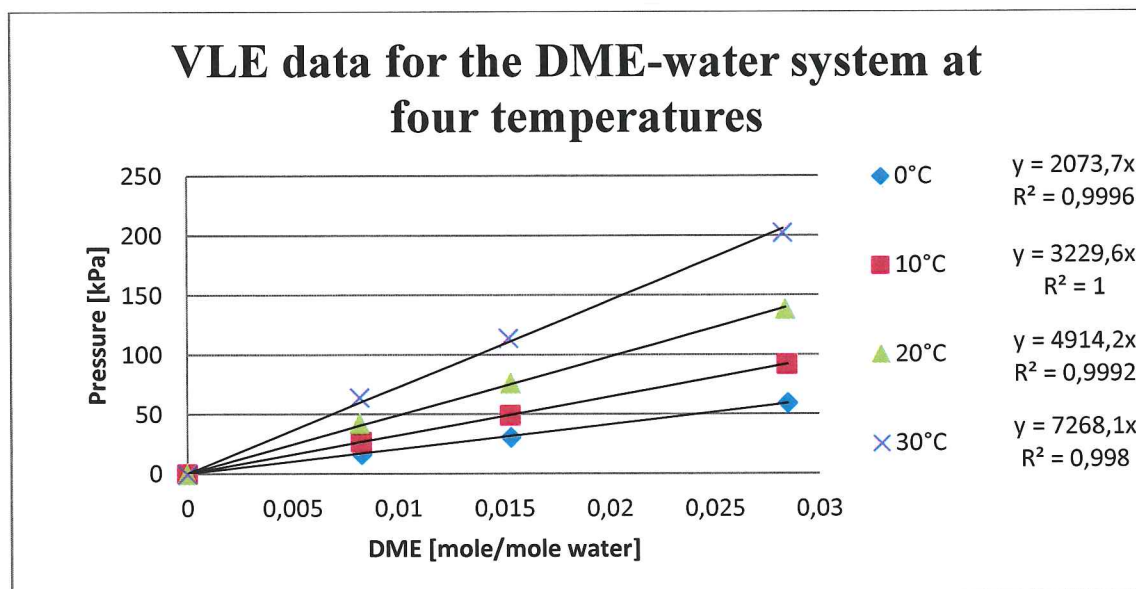
Vapour pressure data at different temperatures from [20]

T [11]	P kPa
273,22	267,41
278	315,19
287,94	434,55
292,93	506,08
297,6	580,96
303,01	677,34
312,95	885,28

Vapour pressure data at different temperatures from [21]

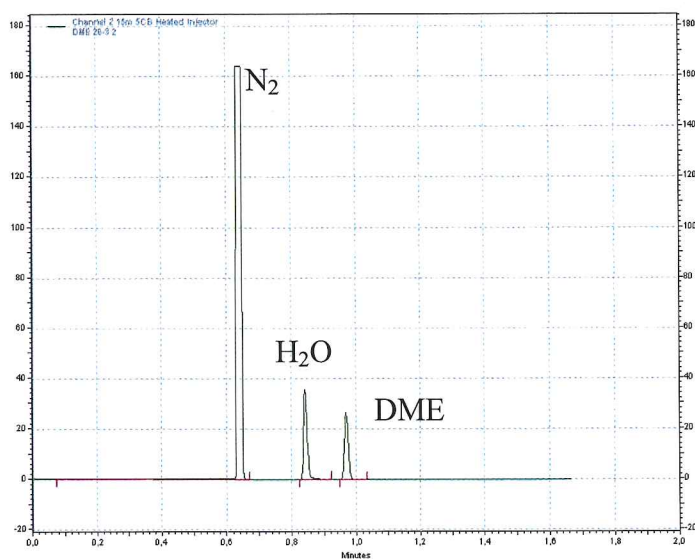
T [11]	P kPa
273,167	266,5
278,16	316,12
283,16	372,9
293,165	509,01
298,084	588,17
303,151	679,68
313,166	889,98

Appendix 5. Vapour-Liquid equilibrium data from the DME-water system at four temperatures

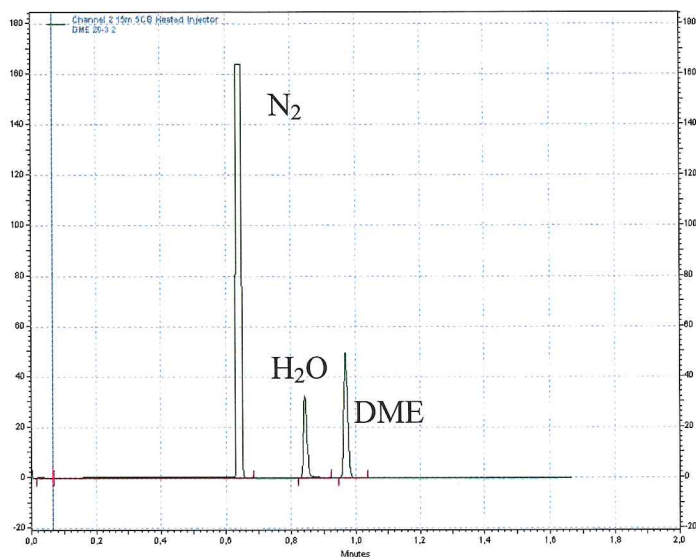


Vapour-Liquid Equilibrium data for the DME-water system at four different temperatures

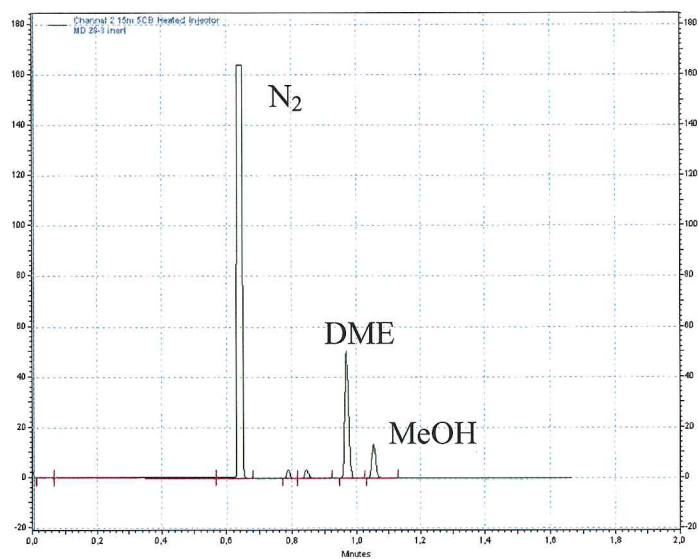
Appendix 6. Chromatograms from experiments



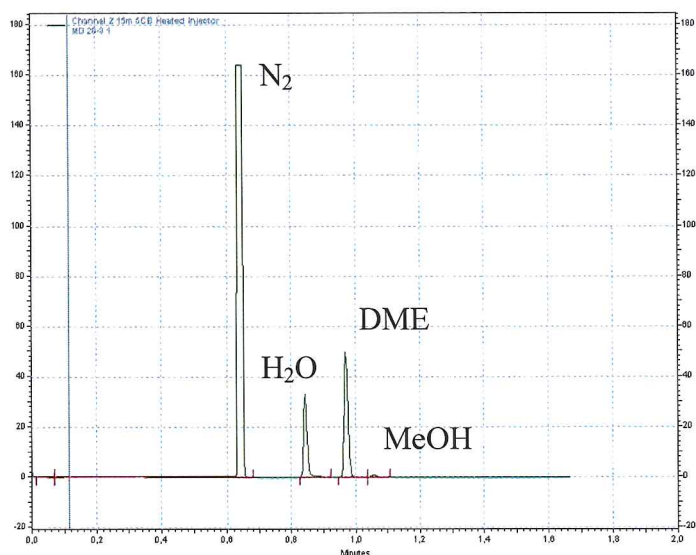
Chromatogram showing DME and water early in a run



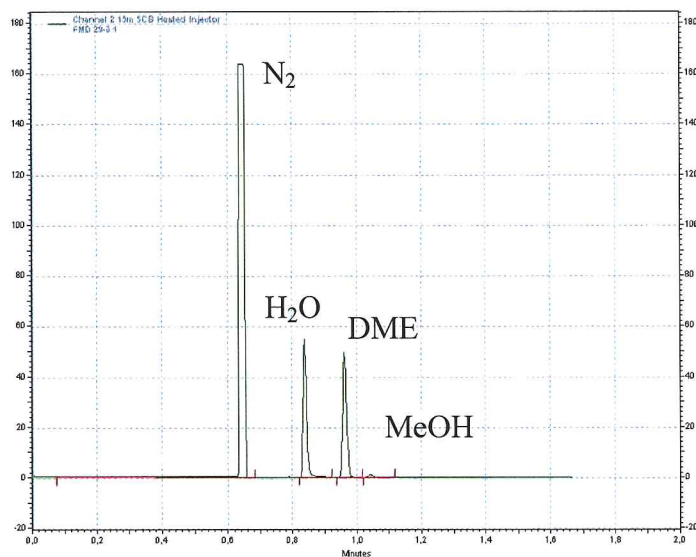
Chromatogram showing DME and water late in a run



Chromatogram showing DME and MeOH with inerts



Chromatogram showing DME, water and MeOH in a regular run



Chromatogram of a run with DME, MeOH, water and FA

Area of the peaks from the previous figure

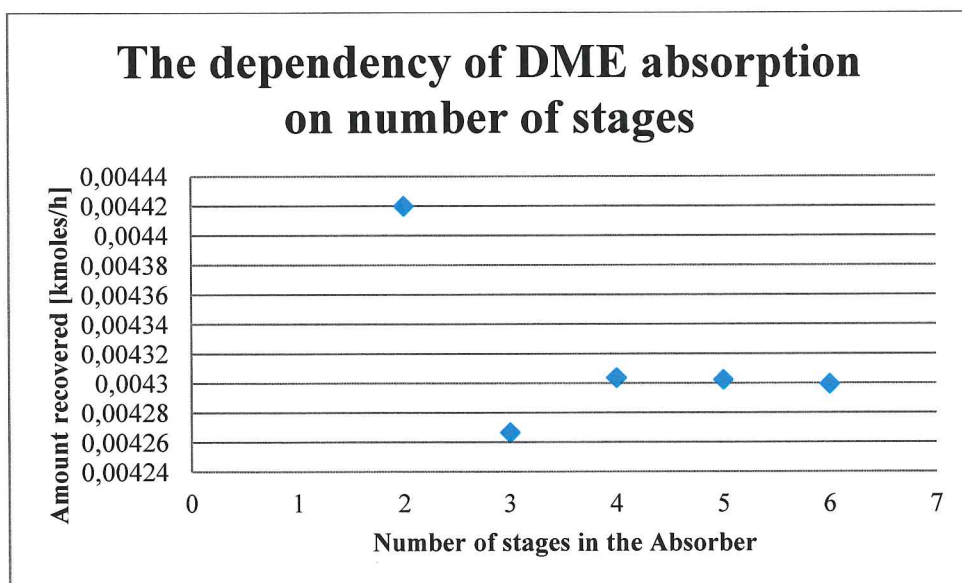
Channel 2 15m

5CB Heated

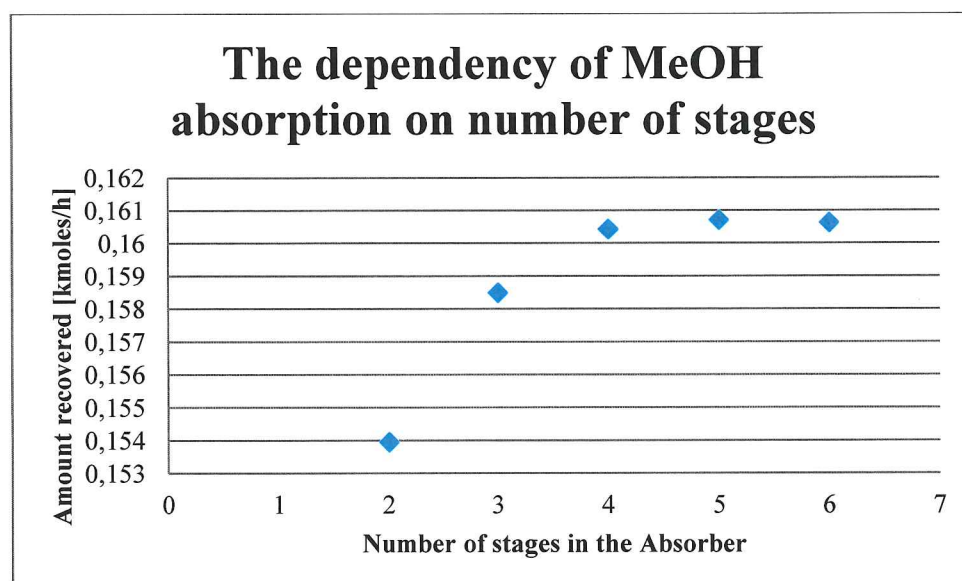
Injector Results

	Retention Time	Area	Area %	Height	Height %
N ₂	0,643	20290910	71,23	16378078	60,88
H ₂ O	0,838	4058151	14,25	5462337	20,30
DME	0,962	4050195	14,22	4960544	18,44
MeOH	1,042	87919	0,31	103454	0,38
Totals		28487175	100,00	26904413	100,00

Appendix 7. The dependency of DME and MeOH absorption on number of stages

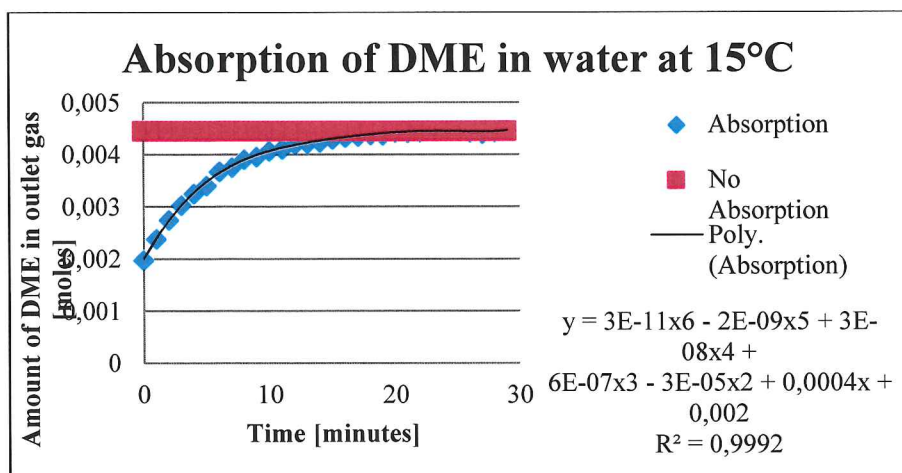


Results from the investigation on the dependency on number of stages for the absorption of DME

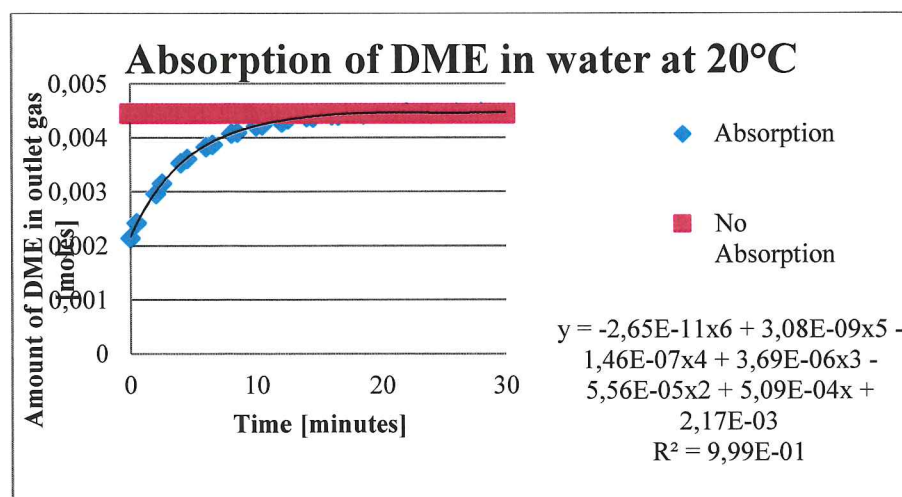


Results from the investigation on the dependency on number of stages for the absorption of MeOH

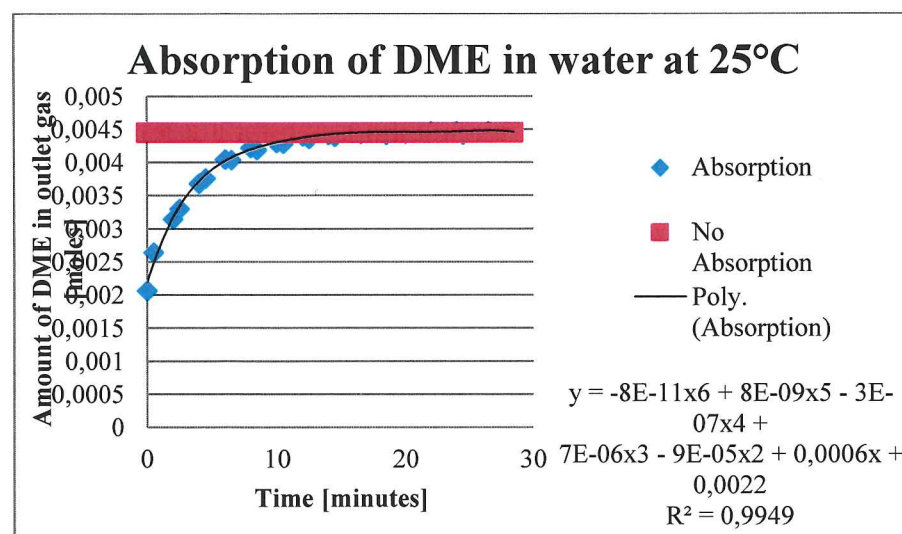
Appendix 8. Plots of experimental results



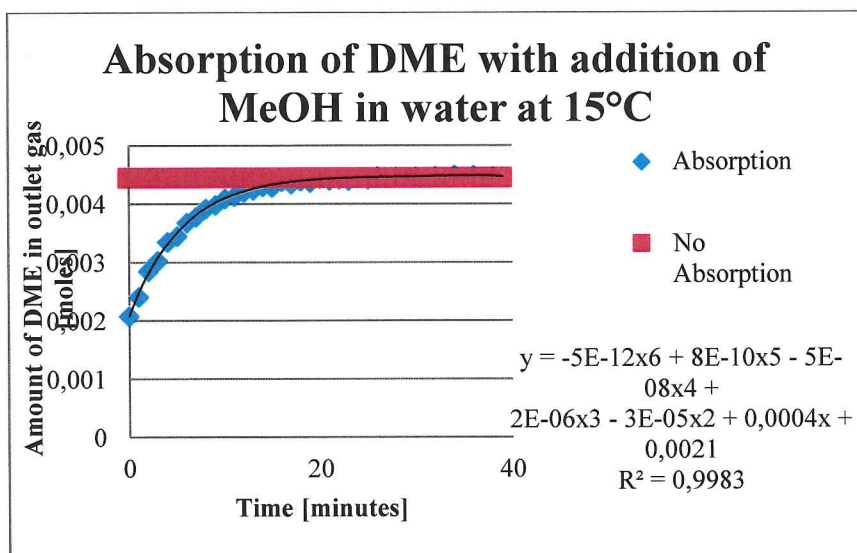
Experimental data with equilibrium line and trend line for DME-water system at 15°C



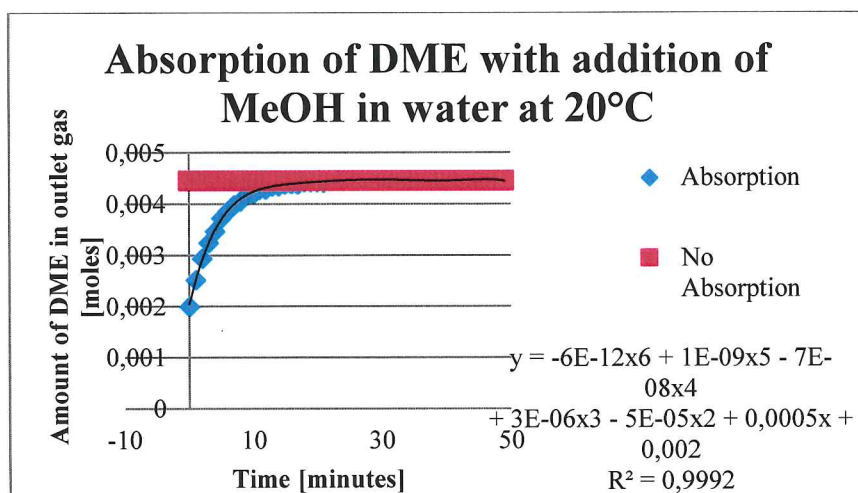
Experimental data with equilibrium line and trend line for DME-water system at 20°C



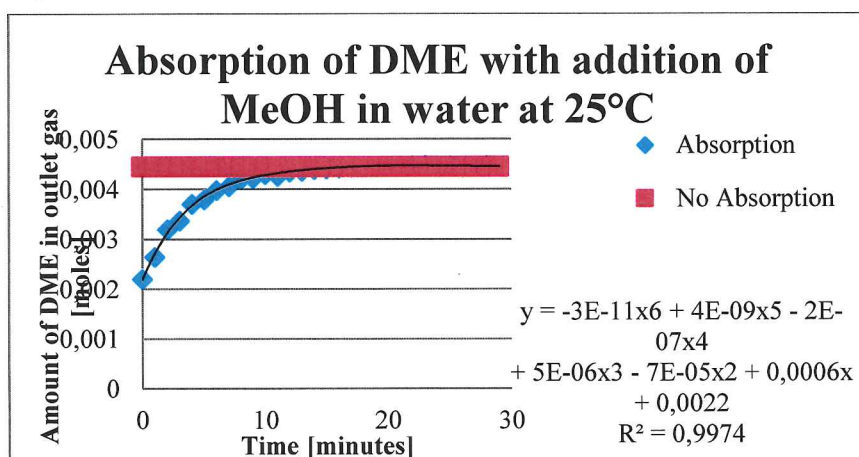
Experimental data with equilibrium line and trend line for DME-water system at 25°C



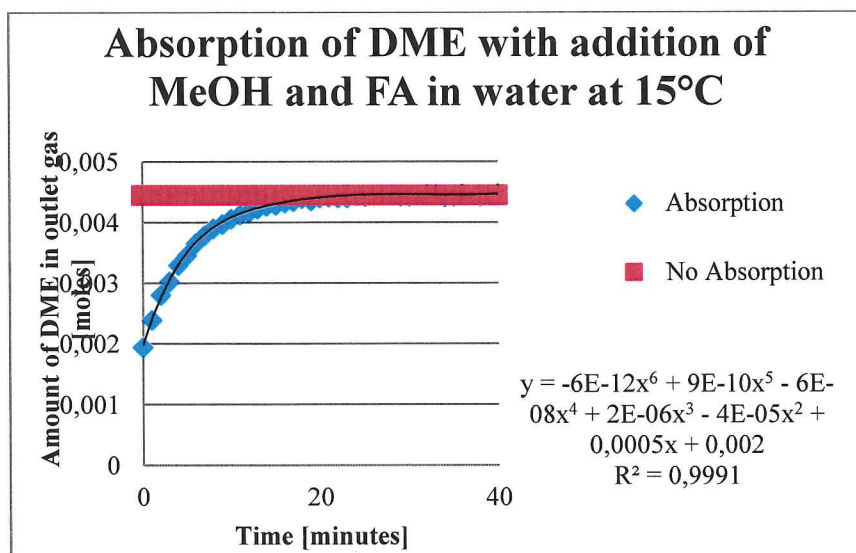
Experimental data with equilibrium line and trend line for DME-MeOH-water system at 15°C



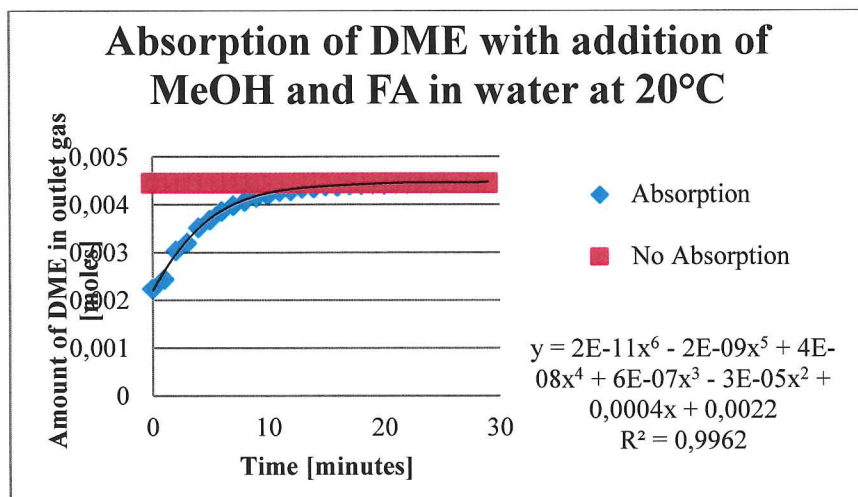
Experimental data with equilibrium line and trend line for DME-MeOH-water system at 20°C



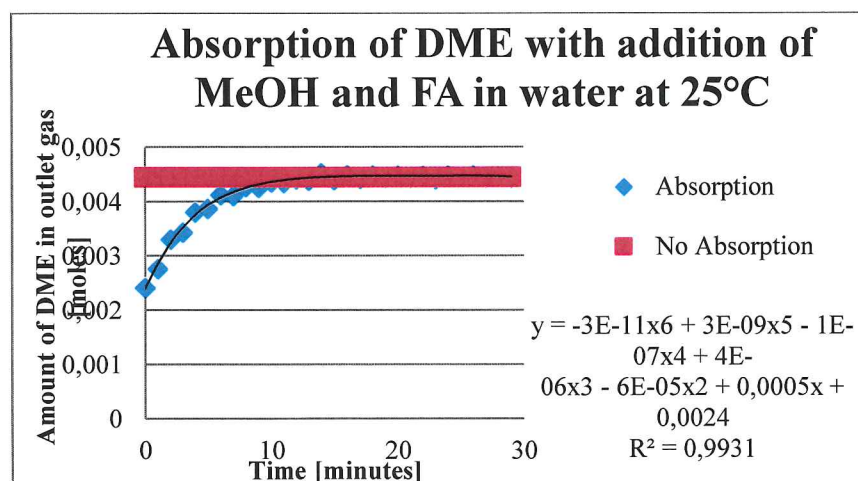
Experimental data with equilibrium line and trend line for DME-MeOH-water system at 25°C



Experimental data with equilibrium line and trend line for DME-MeOH-FA-water system at 15°C



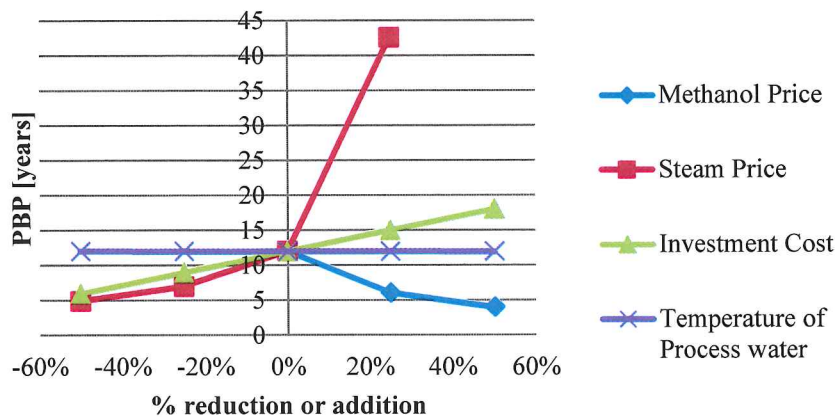
Experimental data with equilibrium line and trend line for DME-MeOH-FA-water system at 20°C



Experimental data with equilibrium line and trend line for DME-MeOH-FA-water system at 25°C

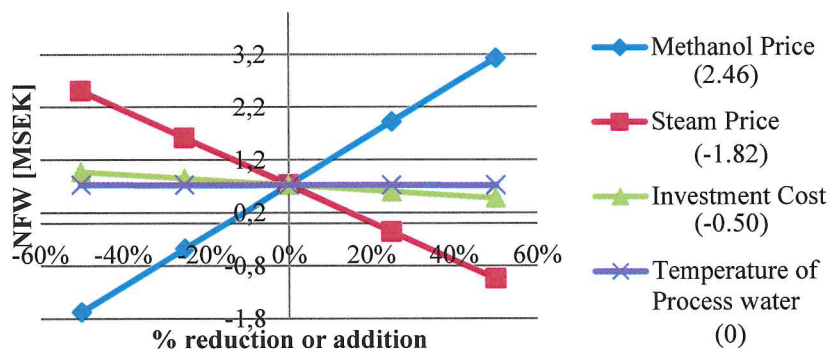
Appendix 9. Sensitivity analysis plots

PBP Full FA absorption case



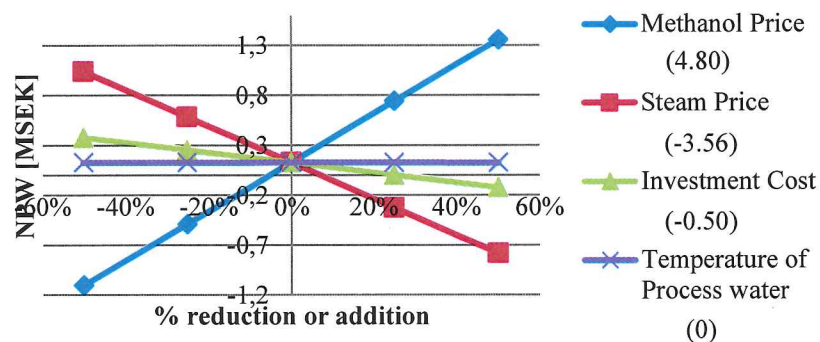
Sensitivity analysis of the PayBackPeriod for the Full FA absorption case

Net Future Worth Full FA Absorption

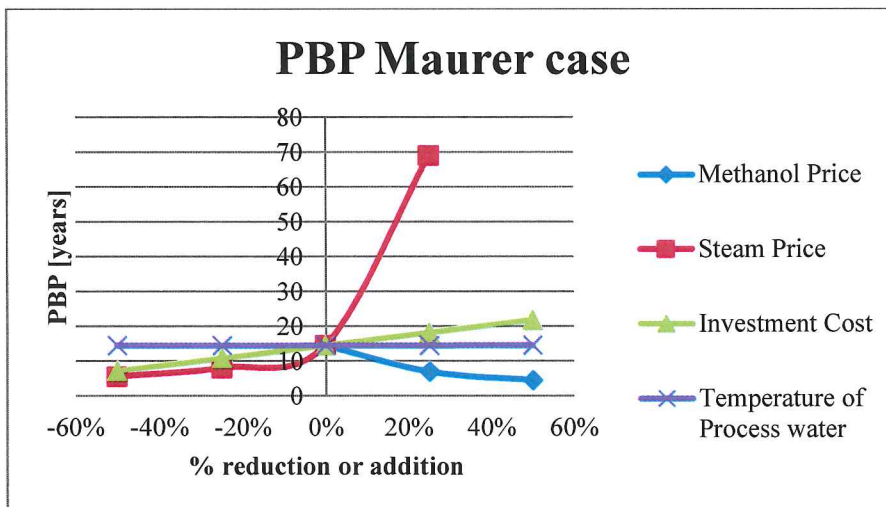


Sensitivity analysis of the Net Future Worth for the Full FA absorption case, slopes included below the series legend

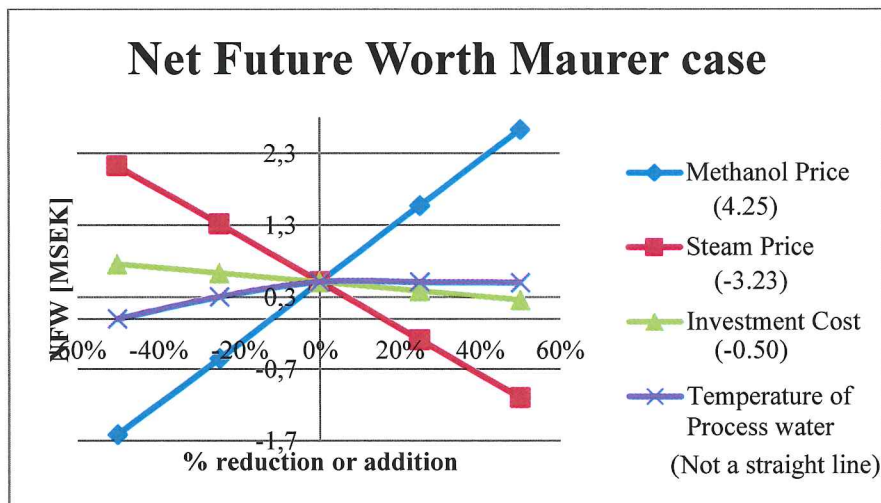
Net Present Worth Full FA Absorption



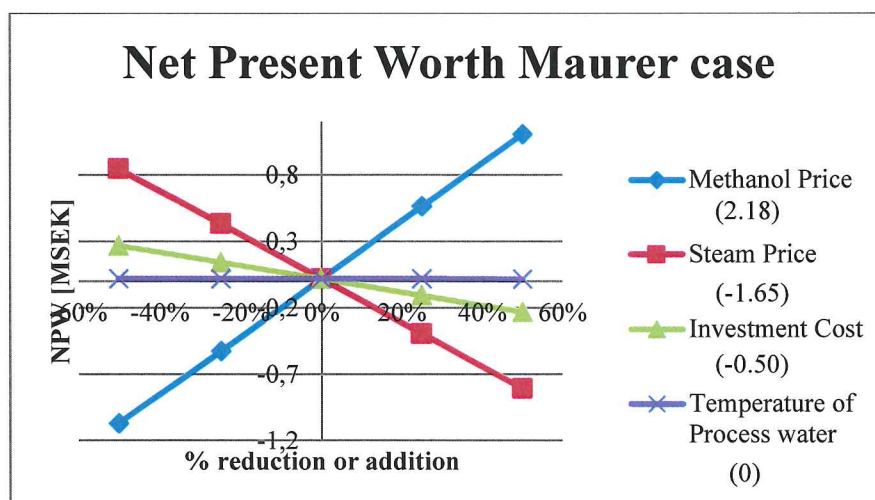
Sensitivity analysis of the Net Present Worth for the Full FA Absorption case, slopes included below the series legend



Sensitivity analysis of the PayBackPeriod for the Maurer based case



Sensitivity analysis of the Net Future Worth for the Maurer based case, slopes included below the series legend



Sensitivity analysis of the Net Present Worth for the Maurer based case, slopes included below the series legend