



TKP4171 PROCESS DESIGN PROJECT

Title: A Comparison of Training Simulators for the Formox Process	Keyword (3-4): Formaldehyde Formox Process Training Simulator HYSYS vs. CHEMCAD
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EXTRACT OF WORK AND CONCLUSIONS Postulations and dimension of work: The intention of this work was to model the Formox process in HYSYS, and compare the simulation with an already existing model in CHEMCAD, to see which one would be most suitable for this formaldehyde process. The models were compared in regards to economical and technical aspects, where the main focus was on usability and benefits, from a beginner's point of view. A literature study was also conducted, to get a better understanding of the benefits of incorporating Operator Training Simulators in the industry.	
Conclusions and recommendations: From a beginner's perspective, CHEMCAD seems to be the better choice when it comes to the Formox process, because it already contains suitable fluid packages and are economically beneficial. However, HYSYS appear to be the better software for process simulation in general, especially when looking at usability.	
Date and signature:	

Preface

This project was given by the Norwegian University of Science and Technology (NTNU), Faculty of Natural Sciences and Technology, Department of Chemical Engineering in cooperation with Perstorp. The project was conducted during the course TKP4171 Process Design Project in the period from 21st of January to 19th of April.

We would like to thank our supervisor Sigurd Skogestad for constructive advise during this project, as well as Vladimiro Minasidis for all the guidance with the simulation software. We would also thank Oleg Pajalic and Krister Forsman at Perstorp for their guidance throughout this process.

NTNU, Trondheim, 19.04.13

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Abstract

Aspen HYSYS simulation software was used for the process simulation of a Formox formaldehyde plant, one of the factories located at the industrial park in Perstorp, Sweden. The Formaldehyde-Methanol-Water system is highly non-ideal, which made it difficult to find a suitable thermodynamic model. Several different fluid packages were tested, and NRTL was chosen. To obtain a product within the same range as the reference values from CHEMCAD, some specifications in the simulation model were adjusted. The total flow rate of the product stream was 8923 kg/h, with a composition of water, formaldehyde and methanol of 51.8 wt%, 47.9 wt% and 0.29wt%, respectively. These values had less than 0.2% deviation from the CHEMCAD reference values.

Perstorp is currently using CHEMCAD chemical process simulation software to model their formaldehyde process. HYSYS and CHEMCAD simulation software were compared with respect to usability, design and costs. From a beginner's perspective, CHEMCAD seemed to be the better choice when considering the Formox process, but in terms of usability, HYSYS were preferred.

The economic perspective of using Operator Training Simulators was looked into. The profit of using a simulator made in HYSYS were calculated, and the result showed an expense of approximately 68 000 NOK. The calculations were estimates and had a high degree of uncertainty. If an equivalent simulator were built in CHEMCAD, the total investment cost would be cheaper than HYSYS. The profit of develop and use a simulator made in CHEMCAD were calculated to approximately 126 000 NOK.

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List of Symbols

BPW	Boiling Point Water
HOC	Hayden-O'Connell
HTF	Heat Transfer Fluid
NC	Not converged
NRTL	Non-Random Two Liquid
OTS	Operator Training Systems/Simulators
P&ID	Piping and Instrumentation Diagram
PFD	Process Flow Diagram
PSRK	Predictive Soave-Redlich-Kwong
R&D	Research and Development
SBM	Simulation Basis Manager
UNIFAC	UNIQUAC Functional-group Activity Coefficients
UNIQUAC	Universal Quasi Chemical
VLE	Vapor-liquid-equilibria

1. Introduction

The commercial production of formaldehyde started in Germany in the 1880s. In the 1920s the production of formaldehyde from methanol and air was introduced and brought the production to an industrial scale (ICIS, 2013). Today there are two main paths to synthesize formaldehyde from methanol. The most common synthesis is performed with a silver catalyst, which gives a complete reaction of oxygen. This process is operated at atmospheric pressure and at temperatures between 600-650°C (Sanhoob, Al-Sulami, Al-Shehri & Al-Rasheedi, 2012). A mixture of vaporized methanol, air and steam reacts over the catalyst and formaldehyde is formed by the dehydrogenation of methanol in an endothermic reaction. The other production path is performed with a catalyst of molybdenum and iron oxide in the temperature range of 270 - 400°C. Vaporized methanol is oxidized in a highly exothermic reaction with air in the presence of the metal oxide catalyst. This process is referred to as the Formox process and gives almost complete methanol conversion (ICIS, 2013). This project is done in cooperation with Perstorp Holding AB, who until recently was the owner of Formox AB a leading supplier of the latter technology including the catalyst, plant design and license.

Perstorp Holding AB has its headquarters in Perstorp, Sweden, where one of the company's largest industrial parks are located. This industrial park started operating in 1881 and today their main products is basic and speciality polyols, catalysts, formats, organic acids and formaldehyde (Perstorp Winning Formulas, 2013b). Perstorp Holding AB sold Formox AB to Johnson Matthey Plc on 28 March 2013. Formox AB is responsible for the installation of 120 formaldehyde plants worldwide (Perstorp Winning Formulas, 2013a).

In this project, Aspen HYSYS simulation software was used for the process simulation of Perstorp's factory number five, one of the factories located at the industrial park in Perstorp. Perstorp is currently using MiMiC and CHEMCAD chemical process simulation software to model their formaldehyde process. The intention of this work was to compare pros and cons of CHEMCAD and HYSYS simulation software. The comparison include usability, design and costs. This project also looked into the economic aspect of using simulation software to model the formaldehyde process. Extending the intervals between every plant turnover and start-up/shut-down is a part of maximizing the profitability of the companies. In order to achieve this, the companies might benefit from developing and use of simulators.

2. Benefits of Simulation Models

In the industry today the development of technology and technological solutions is fast, and it is important for companies and their employees to keep up and be a part of the progress. Operator Training Systems (OTS) has been implemented and become a reality for many companies and processes. The technological development during the last ten years has made simulators for training engineers and operators common, and is considered a necessity in the development of the entire industry (ION, 2010).

An OTS represents the real process system under all system conditions, and lets the operators and engineers practice on rapid changes and how to operate the power system up to its limit (Spanel et al., 2001). The job descriptions of engineers and operators are diverse and the processes and plants are complex. Therefore, it is essential that they understand and have knowledge about the process design and the control system, as well as the normal and abnormal activities (Shephard et al., 1986). These engineering process simulators are an effective way to educate engineers of today and the future engineers. By using simulators, the engineers can study and test ideas before implementing it on the real process, as well as investigate different engineering solutions (Ferreira et al., 2012).

The process industry uses simulators to study individual unit operations, multiple connected units and entire plants. The simulators used in the industry today are capable of presenting almost any type of system, such as multicomponent, multiphase and reactive systems (Bezzo et al., 2004). Training simulators are becoming more and more common for training of operators and engineers (Ballaton et al., 2012). It is widely recognized as a tool for emergency training as well as general training (Yang et al., 2001).

According to Roe et al., (2010), half of the errors and serious incidents caused by humans can be avoided by using simulators when training the engineers and operators. The most severe accidents happens when plants experience unusual situations, therefore it is important that operators and engineers are prepared (Yang et al., 2001).

To ensure that operators and engineers are familiar with process operations out of the ordinary, such as process upset and emergency procedures, the different companies needs to develop simulators for training (Roe et al., 2010). According to Yang et al. (2001), 28% of the largest

property damage losses over the past 30 years in industries involved in hydrocarbon processing, are due to operational error or process upset. Learning by doing and learning based on experience and experiments are a crucial way to develop the competence of engineers and operators (Ferreira et al., 2012).

Another purpose of using these simulators is to avoid unexpected incident costs, by validating procedures, shortening the start-up time, shorter commissioning and increasing the profitability (Roe et al., 2010). The time intervals between complete plant turnovers and shut-down/start-up is extending, which will lead to maximizing of the companies profitability (Yang et al., 2001). In addition to this, the start-up time can be reduced by up to 10% (Roe et al., (2010). The cost of implementing these training systems is based on that fewer delays occur and the system nearly pays for itself. To maintain the OTS and the value of the system it needs to be validated and analysed continuously. It is crucial that the simulators are updated when the real life process is updated. The implementation of a training simulator and maintaining it is highly dependent on commitment and resources from companies and staff (Roe et al., 2010).

Simulators can be used for dynamic modelling and simulation, as well as steady state simulations (Bezzo et al., 2004). The dynamic simulation is based on a steady state model. There are a number of different parameters that needs to be specified, such as actual size of the process equipment, the calculation of process/plant hold-ups, tuning constants of the control loops and the overall process phenomena. Both the steady state and the dynamic models are used to improve the performance of the plant. A steady state model can indicate how the control system response and the performance of the whole control loop, but to get a detailed description of the control system and control loop performance, the operators and engineers need dynamic simulations. It is crucial that the process simulator is robust and capable of handling all the modelling equations used in dynamic and steady state simulation (Bezzo et al., 2004).

Dynamic modelling is applied and commonly used for optimization of a chemical process and also when designing a chemical process (Bezzo et al., 2004). By including the dynamics in the simulation model the engineers get a complete understanding of the overall process and system control (Ferreira et al., 2012). A dynamic simulator not only provides a practical training, but also the theoretical aspect of training operators and engineers (Yang et al., 2001).

A dynamic model of a chemical process plant, not only allows the engineers to review the process control of the plant and the equipment, but also how the process is affected by external disturbances. It is important that these process models consist of sensors and control valves, because this equipment is a part of the control system and gives feedback on failures in process equipment (Yang et al., 2001).

The purpose of simulations is that by simulating a process the engineers can follow and view the entire system and its dynamics over time, without having to change, interrupt and affect it. It is important to remember that the decision they make and the actions they take can have a deep impact on the project success indicators involving areas related to cost, risk, quality and schedule. The dynamics of complex processes are not exact replicas of the real system dynamics, but it is an approximation that makes the relationships between different parts of the system possible to understand (Ferreira et al., 2012).

On the market today there are different tools available for both dynamic and steady state simulations. Ideally, it should be easy to switch between the two simulations and therefore it is important that the two models can be simulated in the same tool without changing the environment. In order to include both experienced and non-experienced engineers and operators, it is important that the simulator is easy to use (Bezzo et al., 2004).

3. The Formox Process

3.1 Specification of Feedstock and Product

This chapter contains the specifications of the main feedstock and the product of the Formox formaldehyde process. The application of the product is also presented. Some of the properties of all the components included in the Formox formaldehyde process are given in Table 1.

Table 1. Properties of components used in the Formox process (Aylward & Findlay, 2008).

Component	Molar mass (g/mol)	Boiling point (°C)	Molecular formula
Methanol	32.04	64.7	CH ₃ OH (MeOH)
Formaldehyde	30.03	-19.0	CH ₂ O
Water	18.02	100	H ₂ O
Oxygen	32.00	-183	O ₂
Nitrogen	28.00	-196	N ₂
Carbon Monoxide	28.01	-192	CO
Carbon Dioxide	44.01	-57.0	CO ₂
Dowtherm A	166.0	257	C ₁₂ H ₁₀ + C ₁₂ H ₁₀ O
Argon	39.95	-186	Ar

3.1.1 Feedstock

In the Formox process, methanol is the main feedstock. Methanol is the simplest alcohol and a light liquid, which is very volatile. The liquid is colorless and flammable, and has a distinctive odor a bit sweeter than ethanol (Methanol Institute, 2011a). Because methanol has so many useful characteristics, it can be used in many different processes as an energy resource, or as a component in many consumer goods. In addition to serve as the main feedstock in the formaldehyde production, methanol is also a component in the final product (Methanol Institute, 2011b).

The most important physical properties of methanol are presented in Table 2.

Table 2. *Properties of methanol (Methanol Institute, 2011c).*

Properties of Methanol		
Molecular weight	32.04	g/mol
Specific gravity (25°C)	0.7866	
Vapor pressure (25°C)	16.98	kPa
Boiling point	64.6	°C
Freezing point	-97.6	°C
Viscosity	0.544	mPa·s
Higher Heating Value (25°C and 1 atm)	726.1	kJ/mol
Lower Heating Value (25°C and 1 atm)	638.1	kJ/mol
Purity	99.5-99.99	%

In this particular Formox process plant, methanol has a temperature of 25 °C and a pressure of 7.2 bars. The feed rate is 4850 kg/h. Air and water are also fed to the process. The air inlet has a flow rate of 14021 kg/h with a temperature and pressure of 15 °C and 0.97 bars, respectively. Water is added to the absorber at a flow rate of 2030 kg/h, with a temperature of 25 °C and pressure of 2.5 bars.

According to *Methanex Monthly Average Regional Posted Contract Price History* the price of methanol in April 2013 was about 390 Euro per metric ton, which is equivalent to 2934 NOK per metric ton (Methanex, 2001).

When producing formaldehyde, methanol is mixed with excess air, which reacts over a modified iron-molybdenum oxide catalyst. In the feed, the ratio between methanol and air cannot exceed 1:13 in order to avoid explosions. The gas mixture is non-explosive when the methanol content in the inlet is below 6.5%. However, to obtain the desired product replacing some of the fresh air with process gas from the absorption allows for methanol content above 6.5% without making the mixture explosive (Reuss et al., 2005).

3.1.2 Product

Formaldehyde is an organic compound, which at room temperature is a colorless gas with a stinging odor. The boiling point of formaldehyde solutions containing up to 55 wt% formaldehyde lies between 99-100°C at atmospheric pressure. At low temperatures, formaldehyde is mixable with solvents such as toluene, ether, chloroform or ethyl acetate. The solubility will decrease with increasing temperatures. Formaldehyde solutions have a flash point of 55 – 85°C. The flash point is dependent on concentration and methanol content (Reuss et al., 2005; Gerberich et al., 2000). The thermodynamics of gaseous formaldehyde is given in Table 3.

Table 3. Thermodynamic values of gaseous formaldehyde (Reuss et al., 2005; Gerberich et al., 2000).

Properties of gaseous formaldehyde	
Heat of formation (25°C)	$-115.9 \pm 6.3 \text{ kJ/mol}$
Gibbs energy (25°C)	-109.9 kJ/mol
Entropy (25°C)	$218.8 \pm 0.4 \text{ kJ/mol} \cdot \text{K}$
Heat of combustion (25°C)	-561.5 kJ/mol
Heat of vaporization (-19.2°C)	23.32 kJ/mol
Specific heat capacity (25°C, 1 atm)	$35.425 \text{ J/mol} \cdot \text{K}$
Heat of solution (23°C)	
- in water	-62 kJ/mol
- in methanol	-62.8 kJ/mol
- in 1-propanol	-59.5 kJ/mol
- in 1-butanol	-62.4 kJ/mol
Cubic expansion coefficient	$2.83 \cdot 10^{-3} \text{ K}^{-1}$
Specific magnetic susceptibility	$-0.62 \cdot 10^6$
Vapor density relative to air	1.04
Density (-80°C)	0.9151 g/cm^3
Density (-20°C)	0.8153 g/cm^3
Boiling point (1 atm)	-19°C
Melting point	-118°C
Flammability in air, lower/upper limits	7.0/7.3 mol%
Ignition temperature	430°C

Formaldehyde is a known chemical intermediate recognized for its high reactivity, and that it is a flexible chemical. In the industry, formaldehyde is usually in the form of aqueous solutions. Gaseous and pure formaldehyde is stable, but formaldehyde solutions are very unstable. Monomeric formaldehyde forms a hydrate with water. These hydrates react further with the formaldehyde molecules to form polyoxymethylenes. These will precipitate in solutions with more than 30 wt% formaldehyde. To inhibit this polymerization methanol or other stabilizers are added (Reuss et al., 2005; Gerberich et al., 2000).

Formaldehyde dissolution in water is exothermic and the heat of solution is -62 kJ/mol, which is independent of the concentration of formaldehyde in the solution. The water solution of formaldehyde, often called formalin, contains different amounts of methanol. The formaldehyde content varies between 25-56 wt%, while the methanol content lies between 0.5-15 wt%. The variations in the methanol content is a result of incomplete conversion during the production of formaldehyde. The product in the Perstorp Formox process has a formaldehyde content of 50 wt% and methanol content between 0.5-1.5 wt% (Reuss et al., 2005; Gerberich et al., 2000).

Formaldehyde solutions are corrosive to carbon steel. Therefore, containers for storage or transportation of formaldehyde are mostly made from stainless steel. It is crucial that these containers can maintain a certain temperature, since formaldehyde solutions precipitate paraformaldehyde when the temperature decreases and/or when the concentration increases. In addition, when the temperature gets to high, formation of formic acid occur. Stabilizing with methanol allows companies and transporters to store solutions for longer times and at lower temperatures (Reuss et al., 2005; Gerberich et al., 2000).

Application of product

Formaldehyde is an important chemical and it is used in the making of industrial products and commercial articles. The manufacturing of urea-, phenol- and melamine-formaldehyde resins is the largest user of formaldehyde in the industry today. These resins are used in the formation of impregnating and adhesives resins, which are mostly used in the manufacturing of plywood, furniture and practical boards. Formaldehyde is a valuable intermediate and around 40% of the total production is used as an intermediate in the manufacturing of other chemical compounds. Formaldehyde is a very important aldehyde and in most cases cannot be replaced (Reuss et al., 2005; Gerberich et al., 2000).

3.2. Process Description

The Formox formaldehyde process is widely used all over the world. There are many reasons for this, where the most important ones are probably the high yield that this process gives, the high formaldehyde concentration and the low content of methanol in the product. Other factors that contribute to the success of the Formox process are the high steam production, high level of safety, the simplicity and reliability of the process, in addition to low operating cost. This process is also environmental friendly (Formox, n.d. a).

3.2.1 Catalysts

In the Formox process a metal oxide is used as a catalyst. The metal oxide is a mixture of iron and molybdenum and the atomic ratio of Mo:Fe is 1.5-2.0. Small amounts of V₂O₅, CuO, Cr₂O₃, CoO, and P₂O₅ are also present. The catalyst is dispersed on an inert support. The catalyst has two active sites: the metal-site, where absorptions occur directly on the molybdenum atom, and the oxygen-site. In the process a two-step oxidation reaction occurs. When converting methanol to formaldehyde the catalyst is reduced. The oxygen content in the feedstock will then oxidize the catalyst and prepare it for a new methanol molecule. A catalyst of this type usually has an effective lifetime of between 12 – 18 months. The overall methanol conversion in the Formox process ranges from 95 – 99% and is dependent on the catalyst selectivity, activity and temperature (Reuss et al., 2005; Gerberich et al., 2000).

The catalyst used in the Formox process is specially made for the process. It has high catalyst selectivity, even at the low reaction temperature during the formation of formaldehyde. They have a high production rate, low pressure drop, low sensitivity to interruptions in the operation and to methanol contaminants as well as a long operating life (Formox, n.d. d).

3.2.2 Reactions

In the Formox process vaporized methanol is mixed with air in the reactor and formaldehyde is formed. The reaction is described by reaction (1).



The methanol is absorbed on the active site on the catalyst, which in this case is on the surface of the Mo-atom. The reaction on the catalyst surface involves two sites. The methoxy-group (-OCH₃) will absorb on the metal-site and the hydrogen will absorb on the oxygen-site.

The rate of reaction (1) is independent of the partial pressure of formaldehyde. The activation energy is measured to 98 ± 6 kJ/mol, and the reaction enthalpy is -215 kJ/mol. The rate of reaction for the formation of formaldehyde can be expressed as shown in equation (2) (Reuss et al., 2005).

$$r = kp_{CH_3OH}^x * kp_{O_2}^y * p_{H_2O}^z \quad (2)$$

Where

P = partial pressure of components

r = reaction rate

k = rate constant

x, y, z = reaction order

$$x = 0.94 \pm 0.06$$

$$y = 0.10 \pm 0.05$$

$$z = -0.45 \pm 0.07$$

There are four side reactions in the formaldehyde process, see reaction equations (3) to (6).



Carbon monoxide is formed in reaction (3), and in reaction (4) the formation of dimethyl ether occurs. The formation of these by-products occurs when formaldehyde desorbs from the catalyst at a slower rate. Dimethyl ether and carbon monoxide are formed in a greater extent than the by-products formed from reaction (5) and (6). In reaction (5) formic acid is generated

and carbon dioxide is formed in reaction (6). These two reactions occur outside the reactor after formalin is produced. All the by-products formed in reaction (3) – (6) are undesired.

At atmospheric pressure and between temperature ranges of 270 – 400 °C the conversion of methanol to formaldehyde is almost complete. In other words, the undesired side reactions (3)-(6) will be reduced (Reuss et al., 2005).

3.2.3 Process and Equipment

The process and equipment described in this chapter are based on factory 5 at Perstorp industrial park. The main components in the Formox formaldehyde process are recirculation blowers, prevaporizer, vaporizer, reactor, absorber and heat transfer fluid (HTF) condenser. The equipment used in the Perstorp Formox process must be robust in order to handle a high gas flow (Gerberich et al., 2000). The process flowsheet is shown in Figure 1.

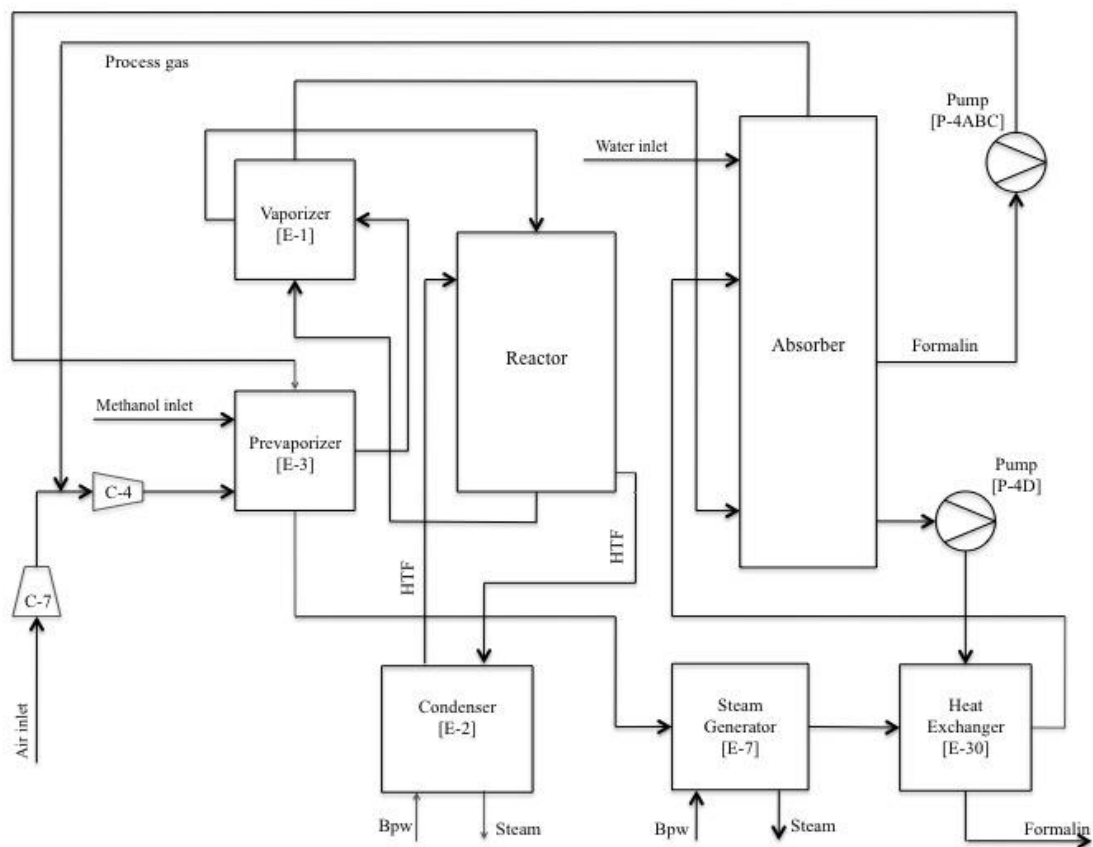


Figure 1. Flowsheet for the Formox process.

Recirculation blowers (C-4ABC)

In the formaldehyde process, three small recirculation blowers, connected in parallel, push the recirculated gas through the process. A frequency converter controls one of these. The other two have no control and only one speed is possible. These two are independent of backpressure and will almost always give the same volumetric flow. Constant conditions on the suction side give a constant mass flow (Perstorp, 2011).

Prevaporizer (E-3)

A prevaporizer is a spiral heat exchanger that heats the methanol to gas. A general spiral heat exchanger is shown in Figure 2. The fluid (A) is added to the middle of the spiral, and is vaporized by adding a heating medium (B) inside the spiral (Perstorp, 2011).

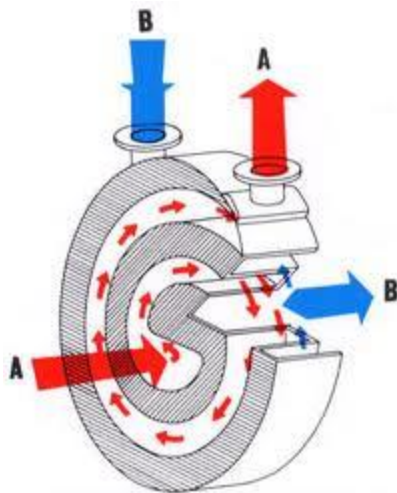


Figure 2. General spiral heat exchanger (JCIM, 2007).

In this process, the heat that is used by the prevaporizer comes from cooling of the absorber. This means that using a prevaporizer in the process is very energy efficient. Process gas goes outside the spiral and formalin circulating from the absorber flows inside. Methanol is sprayed into the heat exchanger together with process gas, where it will be vaporized by formalin (Perstorp, 2011).

Vaporizer (E-1)

Methanol is also sprayed into a vaporizer, which is a shell and tube heat exchanger as shown in Figure 3. Process gas with methanol from the prevaporizer flows inside the tube and hot process

gas from the reactor works as the heating medium. Methanol is then sprayed on the tube plate and heated to gas (Perstorp, 2011).

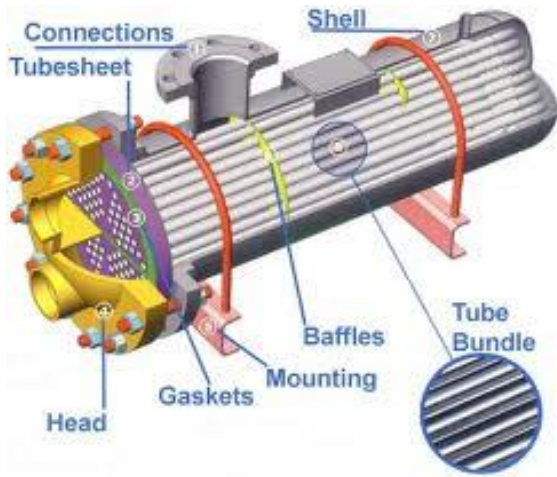


Figure 3. General shell and tube heat exchanger (SEC Heat Exchangers, n.d.).

Reactor (R-1)

The process gas with methanol is fed to reactor where it enters 14600 vertical tubes filled with FeMo catalyst. The tubes are 1400 mm long and have a loading profile that consists of inert (300 mm), mix of inert and pure catalyst (400 mm), pure catalyst (600 mm) and inert (100 mm) from top to bottom. When the gas passes the catalyst, the methanol is oxidized to formaldehyde. This is a very exothermic reaction and consequently a cooling medium is required. The process uses excess air and the temperature in the reactor is isothermally controlled to a temperature of about 340 °C. In this factory a HTF called Dowtherm A is used, which is a mixture of 26.5 % biphenyl and 73.5 % diphenyl oxide. When heat is evolved due to the reaction inside the tubes, the HTF will boil on the outside and vaporize (Perstorp, 2011). When the gas leaves the reactor it is cooled in the vaporizer. After the gas is cooled it is fed to the bottom of the absorption column (Reuss et al., 2005; Gerberich et al., 2000).

Condenser (E-2)

The vaporized HTF from the reactor will flow to the condenser, which has vertical tubes, where it will condense with the use of water. As the HTF cools down, the water will evaporate and

produce steam, which is transported to the steam storage room. The condensed HTF will then flow back to the reactor (Perstorp, 2011).

Absorber (F-5 T1)

The absorber consists of three parts. The lower section includes six valve trays without cooling and can be considered as two theoretical steps. The middle section is a packed section with external cooling by the prevaporizer and vaporizer that are previously mentioned. This section of the absorber can be considered as two theoretical steps. The top section consists of 15 bubble cup trays that have three internal cooling coils on each tray. This section can be considered as three theoretical steps (Perstorp, 2011). The process water fed to the top of the column controls the formaldehyde concentration in the product (Gerberich et al., 2000).

Steam Generator (E-7)

After the recycle stream of formalin from the absorber has passed the prevaporizer, it flows into a steam generator (E-7). Here it is used to heat water at boiling point temperature to create steam. The formalin then passes a heat exchanger (E-30) while the steam is transported to a steam storage room. The steam will be used for other processes at the Perstorp industrial park and contribute to energy savings (Pajalic, 2013a).

Heat Exchanger (E-30)

As stated above, the recycled formalin stream enters a heat exchanger (E-30) before being transported back to the absorber. In the heat exchanger, the formalin product stream from the absorber is cooled down, while the recycle stream is heated (Perstorp, 2011).

3.2.4 Performance

The largest factory at Perstorp is factory five, which have a capacity of 274 tons formaldehyde solution per day (Perstorp, 2011). Table 4 show the performance values per metric ton, which are used at Perstorp when the product contains 37wt% formaldehyde. The amount of methanol shown in the table below gives a molar yield of between 92.6 – 93.7%. One kilogram of catalyst can produce between 20 000 – 30 000 kg formaldehyde before it needs to be replaced (Formox, n.d. b).

Table 4. Performance values for 37 wt% formaldehyde, per metric ton (Formox, n.d. b).

Component	Per metric ton	Unit
Methanol	421 - 426	kg
Electricity (for blower)	55 – 65	kWh
Process water	400	kg
Cooling water	40 – 50	m ³
Catalyst	0.03 - 0.05	kg
Steam produced	450 – 700	kg

3.2.5 Environmental Issues

Formaldehyde is present in the atmosphere and it is released when organic materials combust or in photochemical decomposition. The sources that generate formaldehyde must be divided into two different parts. One part is for the sources that release formaldehyde in defined periods, and the other is for sources that release formaldehyde continuously. In natural processes where sunlight and nitrogen oxides are present, formaldehyde is continuously degraded to carbon dioxide. Photochemical oxidation and incomplete combustion of hydrocarbons is the largest source of formaldehyde present in the atmosphere (Reuss et al., 2005).

Human exposure to formaldehyde comes from engine exhaust, tobacco smoke, natural gas, waste incineration and fossil fuels. Formaldehyde gas causes irritation of the eyes and the respiratory tract, and formaldehyde solutions causes corrosion, skin irritation and sensitization (Reuss et al., 2005).

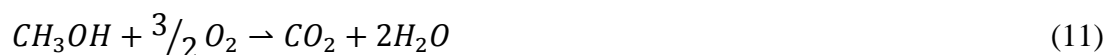
To keep the emission of volatile organic compounds below the legal limits Perstorp has an effective emission control system. This control system makes the Perstorp Formox process the cleanest formaldehyde process in the world (Formox, n.d. e).

3.2.6 Alternative Process

An alternative process for conversion of methanol to formaldehyde is the silver catalyst process. In this process reactions (7) to (9) occur (Reuss et al., 2005).



In this process some by-products are formed from the secondary reactions (10) to (12).



Reaction (8), (9), (11) and (12) is exothermic and the reactions (7) and (10) are endothermic. The overall system becomes slightly exothermic. Around 50 – 60% of the formaldehyde is made by the exothermic reactions (9). The remaining formaldehyde is produced by reaction (7), which is a dehydrogenation reaction and is highly temperature dependent. The conversion varies from 50-99% at a temperature range from 400-700°C. Another factor that affects the conversion and the yield of formaldehyde is the addition of inert components to the reactants. The silver catalyst process is carried out at atmospheric pressure, at temperatures around 600 - 650°C and under strictly adiabatic conditions (Reuss et al. 2005).

In the silver catalyst process the air is sprayed over heated methanol and the vapor and steam is mixed to make the feed. The mixture is sent, via a superheater, to a catalyst bed made up of silver crystals or silver gauze. When the product leaves the catalyst bed, it is rapidly cooled in a steam generator and then in a water-cooled heat exchanger. After the product is cooled, it is passed to the bottom of the absorption tower. In the absorption tower the feed is condensed and tail gas is removed. The remaining methanol and formaldehyde is transported to a distillation tower where it is separated. Methanol is then recycled back to the reactor (Reuss et al., 2005; Gerberich et al., 2000). The process flowsheet is given in Figure 4.

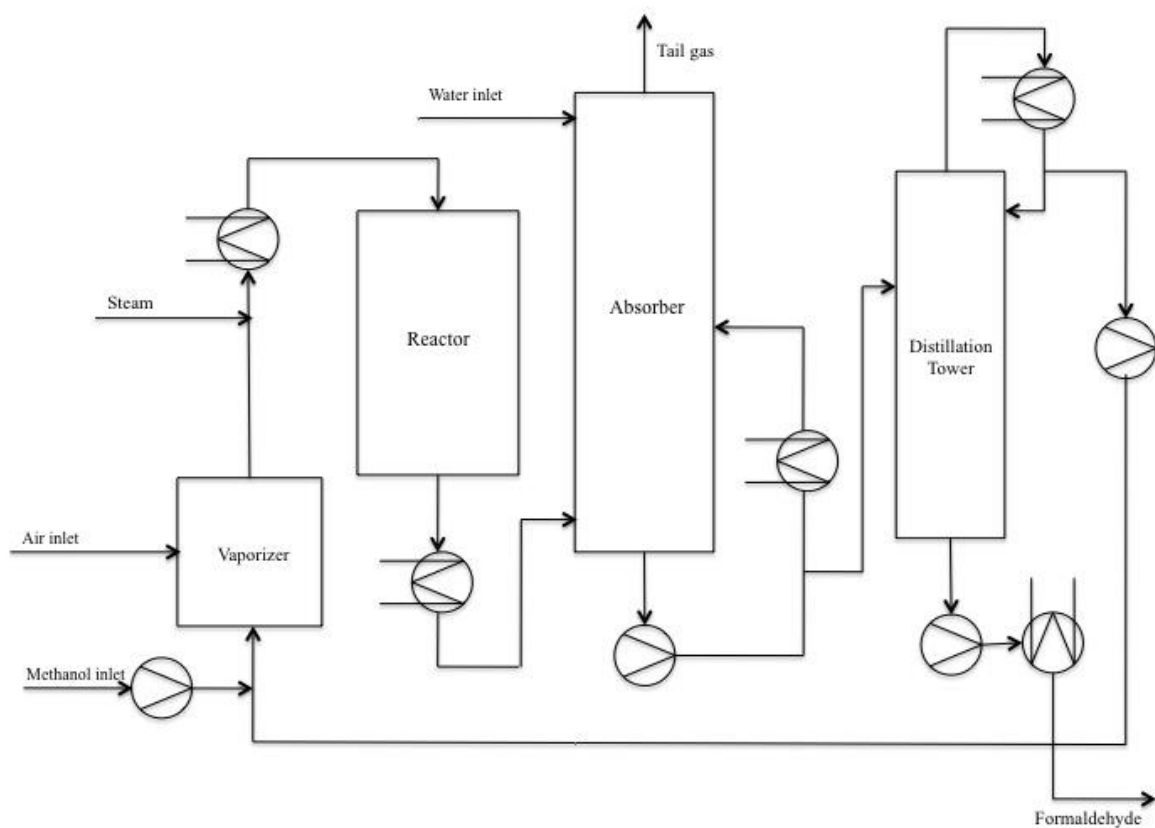


Figure 4. Flowsheet for the Silver Catalyst process.

4. HYSYS Simulation Model

4.1 Steady State Model

A steady state model of Perstorp factory five was built in HYSYS Aspen. The model was made on the basis of a CHEMCAD model of the process, provided by Perstorp, in addition to the Piping and Instrumentation Diagrams (P&IDs) of the factory. The P&IDs of the factory is given in Appendix A.

Fluid Package

The Formaldehyde-Methanol-Water system is highly non-ideal, and the fluid package applied to the model needs to take this into account. The model in CHEMCAD was made with PSRK (Predictive Soave-Redlich-Kwong) as a global thermodynamic fluid package. Maurer fluid package was used locally on each unit operation. PSRK is based on SRK (Soave-Redlich-Kwong), and the package give good results for vapor-liquid-equilibria (VLE) of nonpolar or slightly polar mixtures (Holderbaum, 1991). Maurer is a fluid package, which correlate the VLE in the binary mixtures water-formaldehyde and methanol-formaldehyde. It does this by taking into consideration the physical forces of interaction in addition to chemical reactions (Maurer, 1968).

The PSRK (Aspen properties) was applied to the HYSYS model, but the model did not converge. Maurer was not included in HYSYS, and could therefore not be tested. Aspen technology recommended modelling the vapour phase using the Hayden-O'Connell (HOC) model, which accounts for the strong association in the vapour phase. They recommended modelling the liquid phase by using the UNIFAC (Universal Quasi Chemical (UNIQUAC) Functional-group Activity Coefficients) fluid package with special parameters for interactions between functional groups (Aspen Properties, 2000; AspenTech, 2003). Both UNIFAC and UNIFAC-HOC were applied and tested in HYSYS, but without adding special parameters for group-group interactions. Thus, the results were inadequate.

Sanhoob, Al-Sulami, Al-Shehri & Al-Rasheedi (2012) achieved good results when using a modified version of the thermodynamic package NRTL (Non-Random Two Liquid) when modelling the formaldehyde process in Aspen HYSYS. NRTL is an activity coefficient model

concerning liquid phase, which correlates the activity coefficients of a compound with the mole fractions (Renon, 1968).

Both NRTL and NRTL-general were tested on the HYSYS model. The NRTL-general did not handle formaldehyde as expected. The tests showed that the fluid package ignored the presence of formaldehyde. The tests performed with NRTL fluid package gave reasonable results, but deviations from the reference CHEMCAD values were observed in the streams connected to the absorber.

The fluid packages considered were; NRTL, Wilson and UNIQUAC, and fluid packages with Aspen Properties; NRTL, NRTL-HOC, UNIFAC, UNIFAC-HOC, PSRK, Wilson and UNIQUAC. They were tested on two operation units included in the absorber model. The streams into the units were specified with values obtained from the corresponding streams in the CHEMCAD model. Figure 5, shows the two test objects; one absorption column and one tank.

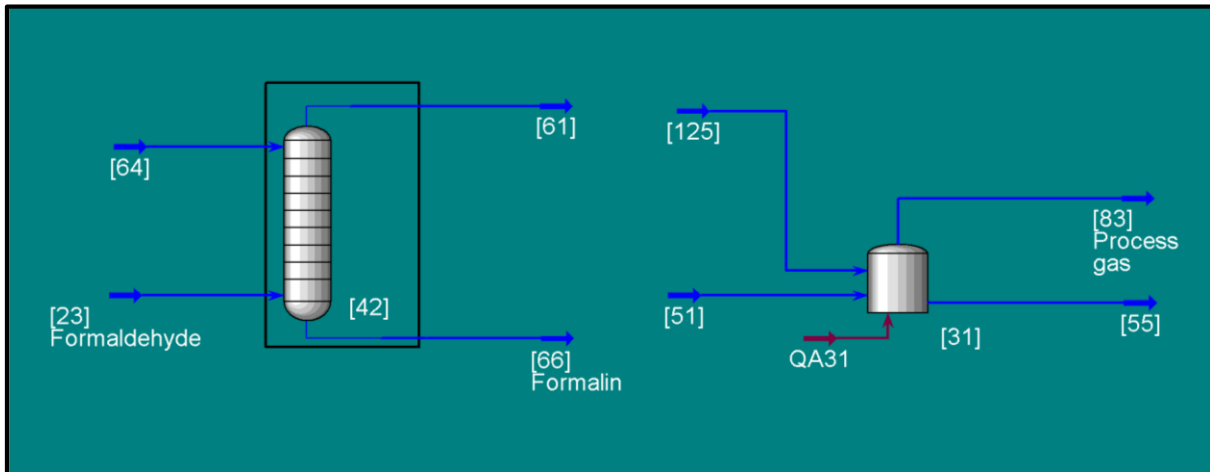


Figure 5. Absorption column and tank used as test objects for fluid packages.

The test result showed that the NRTL fluid package was the best option. The model was built with NRTL even though the thermodynamics in this package was not the same as in the CHEMCAD model. The specifications for the outlet streams [61], [66], [83] and [55], is given in Table 5 and 6 for CHEMCAD (Maurer) and HYSYS (NRTL) respectively. Table 6 also

include the deviation between the reference CHEMCAD values and the ones obtained from HYSYS. The test results for the other fluid packages are given in Appendix B.

Table 5. Specifications of streams [61], [66], [83] and [55] in CHEMCAD, when using Maurer fluid package.

Outlet Streams	CHEMCAD, Maurer			
	[61]	[66]	[83]	[55]
Total flow [kg/h]	49353	8925	38949	2819
Water flow [kg/h]	8944	4621	826	2757
Methanol flow [kg/h]	70.4	25.4	38.8	12.4
Formaldehyde flow [kg/h]	2254	4271	7.50	45.3
Temperature [°C]	76.6	77.7	29.9	29.9
Pressure [bar]	1.36	1.41	1.25	1.25

Table 6. Specifications of streams [61], [66], [83] and [55] in HYSYS, when using NRTL fluid package. In addition, the deviation from reference values (CHEMCAD values) is included.

Outlet Streams	HYSYS, NRTL			
	[61]	[66]	[83]	[55]
Total flow [kg/h]	46066	12211	38933	2835
Water flow [kg/h]	5686	7879	797	2786
Methanol flow [kg/h]	94.3	1.55	40.9	10.3
Formaldehyde flow [kg/h]	2199	4326	17.9	34.9
Temperature [°C]	68.9	70.2	29.9	29.9
Pressure [bar]	1.36	1.41	1.31	1.31
Δ Total flow [kg/h]	-3286	3286	-15.3	15.3
Δ Water flow [kg/h]	-3258	3258	-29.1	29.0
Δ Methanol flow [kg/h]	23.9	-23.9	2.09	-2.09
Δ Formaldehyde flow [kg/h]	-54.2	54.2	10.4	-10.4
Δ Temperature [°C]	-7.69	-7.48	0.00	0.00
Δ Pressure [bar]	0.00	0.00	0.05	0.05

Reactions

Three reactions were added to the model, the reactions are given in equation (1), (3) and (4) in chapter 3.2.2 Reactions. This chapter also describe the kinetics and the thermodynamics. In the CHEMCAD model provided by Perstorp, the kinetics of the reactions were specified differently in each reactor, see Appendix C for exact values. When modelling the reactor in HYSYS both the theory and the specifications made in CHEMCAD were taken into account, but to obtain similar result as the CHEMCAD reference values the specified kinetics had to be manually adjusted. The specifications of the kinetics used in the HYSYS model are given in Appendix C.

The tuning was preformed according to the steady state values, but also at different total mass flow rates. Simulations of the reactor were performed, in both the HYSYS and CHEMCAD model. The feed stream was specified equal to the reference values. Scenarios where the inlet total mass flow rate ranged from 30 000 kg/h to 60 000 kg/h were performed. The results from the simulations are given in Figure 6. The figure present the component mass flow in the product stream of all compounds included in the reactions, as a function of the total mass flow in the feed stream.

The result of simulations of the reactor showed that when adjusting the total flow rate into the reactor the flow rate of the components in the product stream followed the same trend as the reference values. The flow rate of methanol and carbon monoxide did not correspond to the reference values to the same extend as the other components.

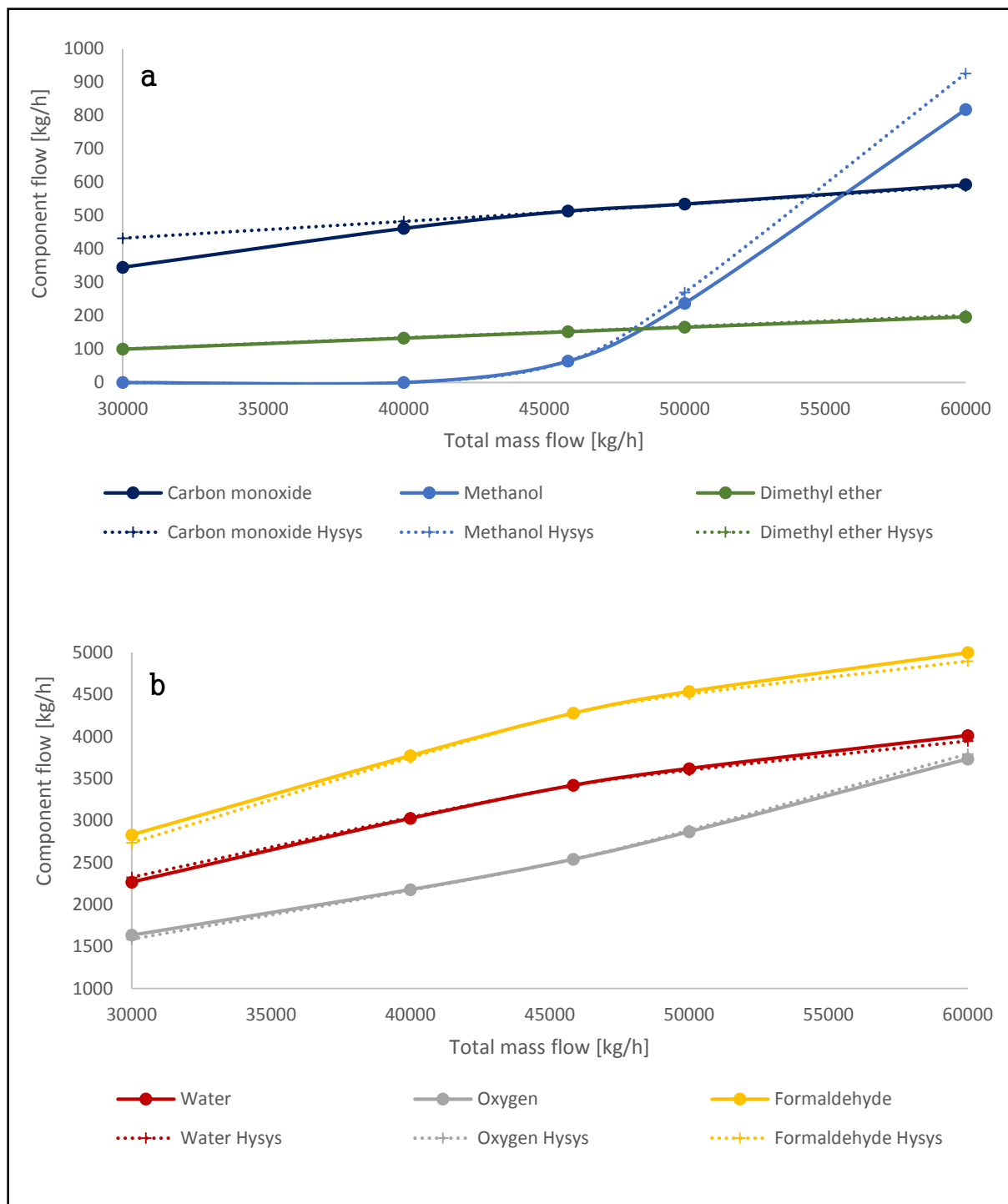


Figure 6. Component mass flow as a function of the total mass flow. Solid lines: CHEMCAD reference values. Dotted lines: result from HYSYS simulation. a: Result for carbon monoxide, methanol and dimethyl ether. b: Results for water, oxygen and formaldehyde.

Equipment

The three small recirculation blowers (C-4ABC) were simplified in the model as one compressor (C-4). The prevaporizer (E-3), vaporizer (E-1), steam generator (E-7) and heat exchanger (E-30), were all modelled as coolers and heaters. The temperature downstream from the operation units were specified and HYSYS calculated the energy stream connected to the unit.

The reactor was modelled as ten separate reactors in Perstorp's CHEMCAD model. In HYSYS the model was made simpler, and one kinetic plug flow reactor was used. Instead of applying the HTF as a cooling medium to the reactor, the outlet temperature of the product stream [18] was specified. In this way, a negative energy stream was added to the reactor and the cycle of the HTF in the condenser (E-2) was left out. Figure 7 *a* and *b*, shows an illustration of how the reactor was modelled in CHEMCAD and HYSYS respectively.

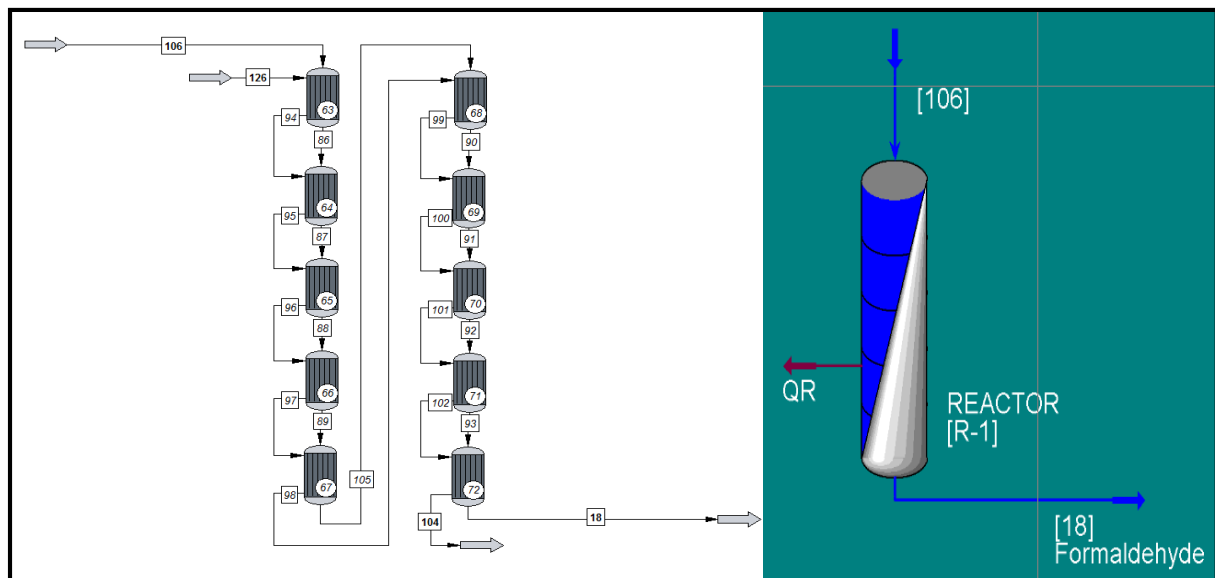


Figure 7. Picture of the reactors in CHEMCAD (a) and Aspen HYSYS (b).

The absorber in the HYSYS model was as in the CHEMCAD model, split into three physically separated parts, as seen in Figure 8. The lower section was modelled as an absorber with two theoretical steps. The middle section was also modelled as an absorber with two theoretical steps, but in this section external cooling was added. An outlet stream, [62], pass through a cooler before re-entering the middle section. The top section was modelled as three tanks with

external cooling. The temperature in the gas outlet was specified in each tank and HYSYS calculated negative inlet energy streams.

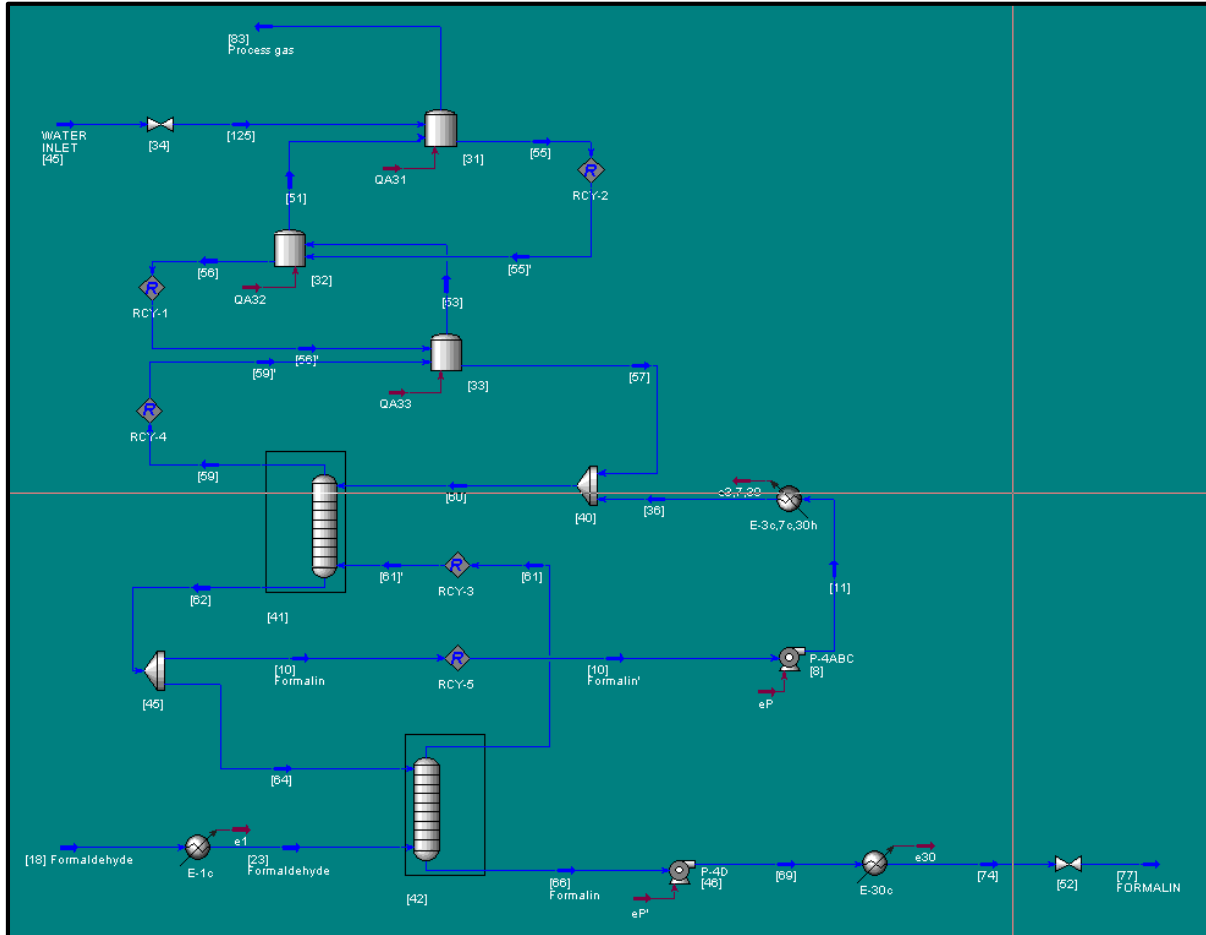


Figure 8. Absorber modelled in HYSYS.

The thermodynamics in the absorber did not correspond well to the CHEMCAD reference values. To obtain a product within the same range as the reference values, some variables were adjusted. Most of the specified temperatures in connections to the absorber were adjusted, as well as the total mass flow of the water inlet and the recirculation stream [127]. This resulted in a much better resemblance for the composition of formaldehyde and water, but the 2.9 wt% of methanol in the reference values were only 0.26 wt% in the HYSYS model. Since the amount of methanol in the product is important to achieve stability, a batch of methanol makeup was added to the product stream. The exact modifications are given in Appendix D. The total mass

flow and the weigh fractions of the final product is given in Table 7. This table also includes the reference values from CHEMCAD.

Table 7. *Composition of the product and the total mass flow obtained in HYSYS, and reference values from CHEMCAD.*

Composition [wt%]	Product, HYSYS	Product, CHEMCAD
Water	51.8	51.7
Oxygen	0.00	0.00
Methanol	0.29	0.29
Dimethyl Ether	0.04	0.08
Formaldehyde	47.9	47.9
Carbon Monoxide	0.00	0.00
Nitrogen	0.01	0.00
Carbon Dioxide	0.00	0.00
Argon	0.00	0.00
Total mass flow [kg/h]	8923	8924

Other simplifications

The air inlet in the CHEMCAD model was manipulated to gain a higher relative humidity and temperature. In HYSYS the values of the preferred state of the air inlet was specified. In this way, no manipulations were further added to the stream. The complete steady state model is presented in Figure 9.

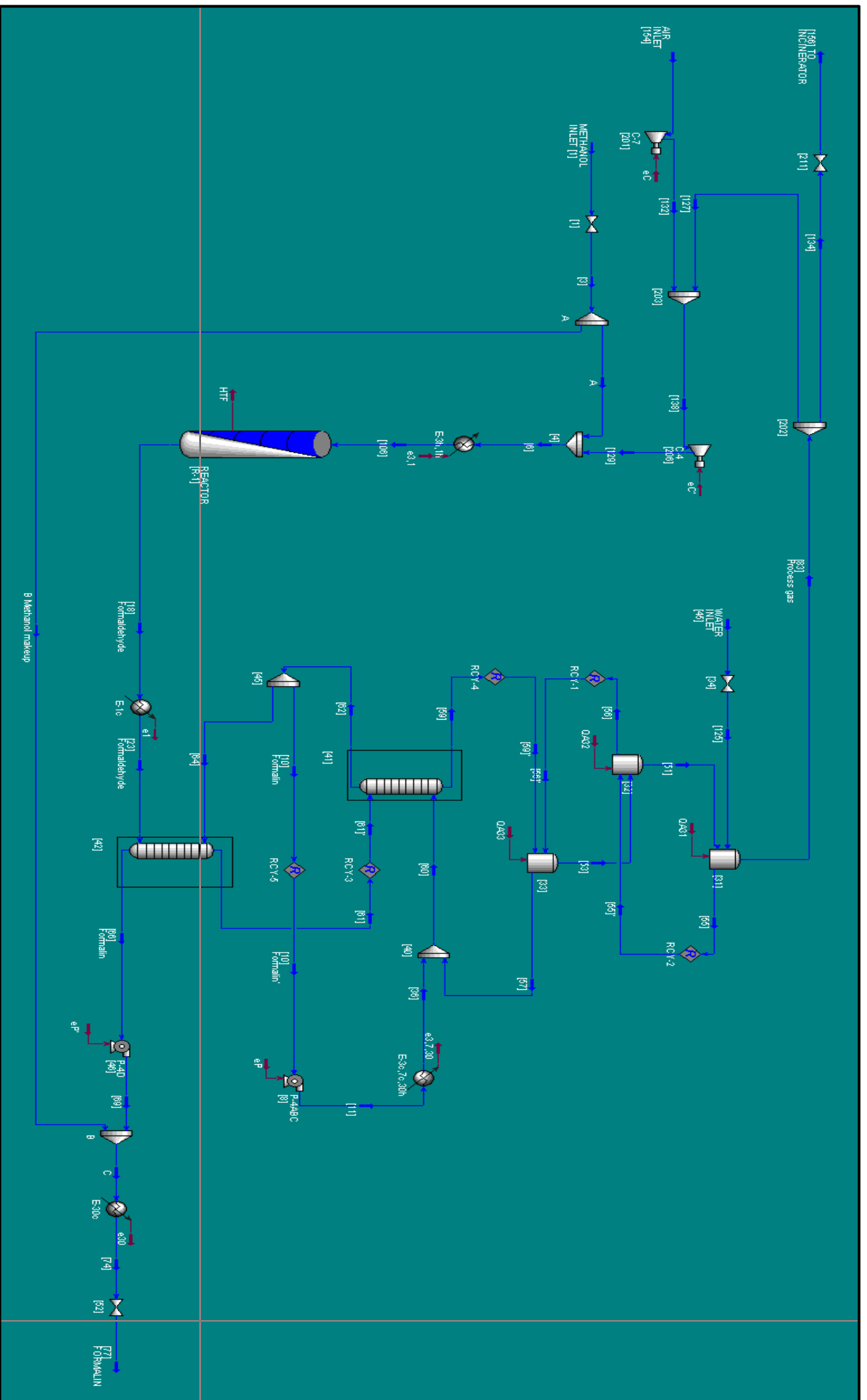


Figure 9. The complete steady state model of the formaldehyde process in HYSYS.

4.2 Dynamic model

The outline of a complex steady state model was made. This was developed more similar to the CHEMCAD model, and some parts of this model could be useful when building a dynamic model. This model is presented in Appendix E.

5. Material and Energy Balances

This chapter includes material and energy balances of the largest units used in the CHEMCAD and HYSYS models. Total balances were set up for the whole system. HYSYS values are compared to CHEMCAD reference values and the deviation between the two is presented (CHEMCAD - HYSYS). All values used for calculating are recovered from the simulation files in HYSYS and CHEMCAD.

As described in chapter 4.1 Steady State Model, many changes were made in the HYSYS simulation file to be able to achieve the correct composition of the product since the thermodynamics were different in the two softwares. Thus, most of the flows deviate from CHEMCAD values.

5.1 Mass Balances

Mass balances of the reactor and absorber are described in this chapter, as well as a total mass balance for the whole system. In addition, mass balances for five internal units in the absorber are given in Appendix F.

5.1.1 Total Mass Balance

The total mass balance of the whole system is presented in Table 8. Three feed streams and two “product” streams are included. Stream [156] is technically not a product stream, but goes to the incinerator. However, since the incinerator is not included in the HYSYS simulation model, it is included as product stream in the total mass balance.

The mass balances in CHEMCAD and HYSYS gives an error of 9 kg/h and 1 kg/h respectively. The error in the HYSYS model is assumed a rounding error, but the error in CHEMCAD has an unknown origin.

The deviations between HYSYS and CHEMCAD are not very large, but stream [1], [45] and [156] differentiate from the CHEMCAD reference values. As described in chapter 4.1, the methanol inlet [1] and water inlet [45] were changed in order to achieve the better correspondence with the product specifications.

Table 8. Total mass balance.

Total Mass Balance						
Comp. [kg/h]	Inlet streams			Outlet streams		
	[154] Air inlet	[1] Met. inlet	[45] Water in.	[156] Incin.	[77] Formalin	
CEMCAD						
H2O	59.2	0.00	2030	254	4617	
O2	3238	0.00	0.00	780	0.008	
Methanol	0.00	4850	0.00	11.7	25.6	
diM-Ether	0.00	0.00	0.00	44.7	6.80	
Formaldehyde	0.00	0.00	0.00	2.26	4276	
CO	0.00	0.00	0.00	158	0.001	
N2	10530	0.00	0.00	10524	0.062	
CO2	8.46	0.00	0.00	8.45	0.001	
Argon	185	0.00	0.00	185	0.003	
Total	14021	4850	2030	11967	8925	
HYSYS						
H2O	59.2	0.00	1850	84.1	4618	
O2	3238	0.00	0.00	776	0.07	
Methanol	0.00	4876	0.00	22.1	26.3	
diM-Ether	0.00	0.00	0.00	47.3	3.15	
Formaldehyde	0.00	0.00	0.00	19.8	4275	
CO	0.00	0.00	0.00	152	0.01	
N2	10530	0.00	0.00	10529	0.76	
CO2	8.46	0.00	0.00	8.45	0.01	
Argon	185	0.00	0.00	185	0.02	
Total	14021	4876	1850	11823	8923	
<i>Deviation</i>	<i>0</i>	<i>-26</i>	<i>180</i>	<i>144</i>	<i>2</i>	

5.1.2 Reactor

Since it was decided to exclude the HTF streams from the HYSYS model and instead use an energy stream out from the reactor, only two streams are part of the reactor mass balance given in Table 9. The deviations between CHEMCAD and HYSYS are the same for both streams, which were expected since there is one stream in and one out of the reactor. The total mass flow in HYSYS, are larger than in CHEMCAD and the mass fractions also deviates. This is mainly due to different composition and flow rate of the recirculation stream in the two models. The table also points to correct calculations since mass is conserved in both models.

5.1.3 Absorber

The overall mass balance for the absorber is given in Table 10. In the HYSYS model there is a rounding error of 1 kg/h, in CHEMCAD the model shows that mass is conserved. The deviation in the water inlet [45] from CHEMCAD to HYSYS is made intentionally to achieve better accordance for the values in product stream [66] Formalin.

Table 9. Reactor mass balance.

Reactor Mass Balance		
Components [kg/h]	Inlet stream	Outlet stream
	[106]	[18] Form.hyde
CHEMCAD		
H2O	632	3419
O2	4995	2537
Methanol	4876	64.0
diM-Ether	101	152
Formaldehyde	5.10	4278
CO	356	514
N2	34251	34251
CO2	27.5	0.00
Argon	601	27.5
Total	45844	45844
HYSYS		
H2O	265	3058
O2	5140	2678
Methanol	4904	76.6
diM-Ether	116	167
Formaldehyde	48.5	4344
CO	373	525
N2	36355	36355
CO2	29.2	29.2
Argon	638	638
Total	47871	47871
<i>Deviation</i>	<i>-2027</i>	<i>-2027</i>

Table 10. Overall absorber mass balance.

Absorber Total Balance				
Components [kg/h]	Inlet streams		Outlet streams	
	[45] Water in	[23] Form.hyde	[83] Process g.	[66] Formalin
CHEMCAD				
H2O	2030	3419	826	4621
O2	0.00	2537	2537	0.008
Methanol	0.00	64.0	38.8	25.4
diM-Ether	0.00	152	146	6.78
Formaldehyde	0.00	4278	7.50	4271
CO	0.00	514	514	0.001
N2	0.00	34251	34251	0.06
CO2	0.00	27.5	27.5	0.001
Argon	0.00	601	601	0.003
Total	2030	45844	38949	8925
HYSYS				
H2O	1850	3058	291	4618
O2	0.00	2678	2678	0.07
Methanol	0.00	76.6	76.4	0.26
diM-Ether	0.00	167	163	3.15
Formaldehyde	0.00	4344	68.2	4275
CO	0.00	525	525	0.01
N2	0.00	36355	36354	0.76
CO2	0.00	29.2	29.2	0.01
Argon	0.00	638	638	0.02
Total	1850	47871	40823	8897
<i>Deviation</i>	<i>180</i>	<i>-2027</i>	<i>-1874</i>	<i>28</i>

5.2 Energy Balances

Energy balances for the reactor and absorber are described in this chapter, as well as a total energy balance for the whole system. In addition, energy balances for compressors, pumps, heaters and coolers are given in Appendix G, as well as the energy balance for five internal units in the absorber.

5.2.1 Total Energy Balance

The total energy balance for the whole process is given in Table 11. There are some values crossed out in the table. These values seemed to belong to the three tanks in the CHEMCAD model, but when applying them to the balances, it becomes clear that they are wrong. Thus, these values are not taken into account. After this correction the energy balance for the CHEMCAD model has an error of -7 MW. This error might occur due to some misinterpretation of the CHEMCAD model provided from Perstorp, or rounding errors. In the HYSYS model the energy balance sums to zero, which points to correct calculations.

The deviations between HYSYS and CHEMCAD are relatively big, but the process was modeled in two very different ways, so this was to be expected.

Table 11. Total energy balance.

Total Energy Balance		
	In [MW]	Out [MW]
CHEMCAD		
Streams		
[154] Air inlet	-0.282	
[1] Methanol inlet	-10.2	
[45] Water inlet	-8.95	
[156] To incinerator		-1.20
[77] Formalin		-29.5
[126] HTF inlet	12.3	
[104] HTF outlet		17.1
[24] CW inlet	-1201	
[30] CW outlet		-1194

Energy streams		
Compressor C-7 [201]	0.0818	
Compressor C-4 [206]	0.544	
Pump P-4D [46]	3.48e-04	
Pump P-4ABC [8]	6.74e-04	
Heaters water system[27-29]	3.00	
Tank [33]		46.7
Tank [32]		8.44
Tank [31]		0.383
Total	-1205	-1198

HYSYS

Streams		
[154] Air inlet	- 0.280	
[1] Methanol inlet	- 10.1	
[45] Water inlet	- 8.13	
[156] To incinerator		- 0.653
[77] Formalin		- 25.5

Energy streams		
Compressor C-7 [201]	0.102	
Compressor C-4 [206]	0.550	
Heater E-3h,1h	3.07	
Reactor [R-1]		4.70
Cooler E-1c		2.33
Pump P-4D [46]	4.235e-05	
Cooler E-30c		0.156
Pump P-4ABC [8]	7.52e-04	
Cooler E-3c,7c,30h		2.42
Tank [33]	0.956	
Tank [32]	- 2.48	
Tank [31]	- 0.237	
Total	- 16.6	- 16.6
<i>Deviation</i>	<i>-1188</i>	<i>-1181</i>

5.2.2 Reactor

The energy balance for the reactor is given in Table 12. The energy balance for the CHEMCAD and HYSYS model has both a small error, which is assumed a rounding error.

There are deviations between HYSYS and CHEMCAD. The table shows that the deviations are mainly in the feed and product streams. This was expected since these flows have different composition and mass flow rate.

Table 12. Reactor energy balance.

Reactor Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[106]	-9.53	
[18] Formaldehyde		-14.4
[126] HTF inlet	12.3	
[104] HTF outlet		17.1
Total	2.77	2.70
HYSYS		
[106]	- 8.22	
[18] Formaldehyde		- 12.9
Energy stream HTF		4.70
Total	- 8.22	- 8.20
<i>Deviation</i>	<i>11.0</i>	<i>10.9</i>

5.2.3 Absorber

The overall energy balance for the absorber is given in Table 13. In HYSYS the model shows that energy is conserved. The model made in CHEMCAD shows a small error of -2 MW. The deviation between the software is difficult to compare because of different specifications.

Table 13. Overall absorber energy balance.

Absorber Total Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[125]	-8.94	
[83] Process gas		-3.90
[23] Formaldehyde	-16.5	
[66] Formalin		-28.5
[24] CW inlet	-1201	
[30] CW outlet		-1194
Heaters water system[27-29]	3.00	
Total	-1224	-1226
HYSYS		
[125]	-8.13	
[83] Process gas		-2.27
[23] Formaldehyde	-15.3	
[66] Formalin		-25.3
Energy stream eP	7.52e-04	
Energy stream e3,7,30		2.42
Energy stream Tank 33	0.956	
Energy stream Tank 32	-2.48	
Energy stream Tank 31	-0.237	
Total	-25.2	-25.2
<i>Deviation</i>	<i>-1199</i>	<i>-1201</i>

6. Comparing CHEMCAD and Aspen HYSYS Simulation Software

This chapter contains information about two simulation software, Aspen HYSYS and CHEMCAD. Pros and cons with both softwares are presented, and a comparison between the two is described, from a new user's point of view.

The purpose of using simulation software such as HYSYS and CHEMCAD is to maximize the efficiency of engineers in the sense that they get a better understanding of the process. Also contribute to them being able to predict how adjustments or changes will influence the process, such as product composition, pressures and temperatures (Hamid, 2007).

Both steady state and dynamic modeling are very important when designing and optimizing a chemical process. The steady state model can be used to maintain energy and material balances and evaluate different plant scenarios. It can also be used for optimizing the process by reducing costs, while maximizing the production. The dynamic model can be used to confirm that the process is actually producing the desired product, and that the production is safe and easy to operate. It can also be used to optimize controller design and provide information about startup and shutdown conditions. All balances that are derived in dynamic mode are similar to the ones found in steady state, except for an addition of the accumulation term. This accumulation term is what allows the output variables to change over time (AspenTech, 2009).

A lot of equipment used in the chemical industry has material inventory or holdup. In such cases, dynamic modeling is a helpful tool. It is not so easy to identify changes in composition, temperature, pressure and flow in an inlet stream just by looking at the outlet stream. It is therefore useful to have a holdup model, which describes how the output stream reacts to changes in input and holdup (AspenTech, 2009).

6.1 HYSYS

HYSYS is an engineering simulation tool that has been used by universities and colleges as a learning tool, especially in chemical engineering. It is also widely used in the industry in research, development, modeling and design (Hamid, 2007).

In HYSYS it is possible to create both dynamic and steady state simulations, and it is possible to evaluate the same model from either perspective. HYSYS is equipped with many operations and designs, which allows simulations of many different processes. HYSYS is able to model processes from the upstream part of the industry, gas processing, refining processes and chemical processes (Hamid, 2007). HYSYS is a quite expensive simulation software, and is mostly used by large companies. One license costs about ████████ NOK per year (Pettersen, 2013; Hillestad, 2013). However, the prize is often negotiated between AspenTech, who deliver the product, and the customer depending on license quantities.

Starting Up

Before building the model in HYSYS, it is very important that the correct fluid package and components are chosen for the specific process. This is done in the *Simulation Basis Manager* (SBM). In the SBM it is possible to add fluid packages, components and reactions.

Selecting Chemical Components

Chemical components are selected by adding them to the list found under the *Components* tab. Here it is easy to add, remove or change the order of the components.

Selecting Thermodynamics

The fluid package is chosen from the list found under *Fluid Pkgs*, where HYSYS has collected a number of packages to choose from. If the components already have been selected, the SBM will state if the chosen package is compatible or not with the components. If there are some uncertainties in which fluid package that are most suitable for the process, the *Property Wizard* can be used for a recommendation. In Aspen HYSYS it is also possible to use fluid packages with Aspen properties. These fluid packages need to be connected to a component list with Aspen properties. In addition, after the global fluid package is chosen and the building of the model has started, a local different fluid package can be applied to the individual unit operations.

Adding reactions

To add the desired reactions in the SBM, simply click on the *Reactions* tab and add the desired reactions. It is also necessary to specify what type of reactions that occur. In HYSYS it is possible to choose from these types of reactions:

- Chemistry dissociation
- Chemistry equilibrium
- Chemistry salt
- Conversion
- Equilibrium
- Heterogeneous catalytic
- Kinetic
- Simple rate

Depending on which type of reaction that is chosen, information must be added for the reaction to be approved. Generally it is necessary to add the components that take part in the reaction, as well as their stoichiometric coefficient.

In order for these reactions to be added to a reactor later in the simulations, it is important to include them in a reaction set. It is therefore necessary to activate the desired reactions for one reactor in the same reaction set. It is also crucial to add the reaction set to the fluid package in order for it to be available in the simulation file.

Design/Layout

The layout of HYSYS consists of a large window with a toolbar where the simulations are created, saved, loaded etc. However, the green PFD-screen where the simulations are made is the main focus. The PFD includes a toolbar with a lot of different tools that is useful when simulating a process. These tools are:

- *Attach Mode* – Enables attaching streams to units by clicking the units instead of having to open them. Colored dots appear for different streams: blue dots = normal stream, red dots = energy stream

- *Auto Attach Mode* – Attaches stream automatically as units are put in the PFD. The stream(s) that are currently marked when adding another unit will automatically be attached to this unit.
- *Size Mode* – allows for sizing the units and streams as desired.
- *Break Connection* – Breaking the connection between a stream and a unit
- *Swap Connections* – Allows for swapping of streams that are connected to the same unit.
- *Drag Zoom* – allows for zooming on streams and units if it is desirable to look at a small part of the simulation.
- *Add Text* – This tool creates a text box where important information can be added directly into the PFD.
- *Quick Route Mode* – Normally when drawing the streams, their lines will avoid the units so that no stream will cross a unit. If it is desirable to have the line go in a certain direction, and perhaps over a unit, this tool can be switched on and the user can decide where the lines will go.
- *Drag Mode* – Normally the cursor cannot drag the simulation around, so if this is desired, the *Drag Mode* tool must be turned on.
- *Object Palette* – includes all available units.

Parameters that can be specified by the user have blue text, while the ones that the software calculates have black text. It is not necessary to include values for all the “blue” parameters, since HYSYS will calculate most of them as well.

HYSYS is designed with color codes, which makes it easier to get an overview of the simulation. Units have three different color codes: red, yellow and green. Red indicates that some crucial information needs to be included. Yellow indicates that there are some details missing, such as temperature, pressure or vapor fraction. A unit can also become yellow if too much information has been added, and the unit is over specified. Units with green color are ok. Streams can have two different color codes: light blue and royal blue. Light blue indicates that the stream needs more information to function, and they will turn royal blue when that information is added.

Choosing Engineering Units

In HYSYS all engineering units are available for all the streams and units. The default units are SI, but while entering units it is possible to change them to other units. HYSYS will then convert them to the corresponding SI-unit.

Adding Streams or Units

As stated earlier, all the units in HYSYS can be found in the *Object Palette*. When the unit is placed in the PFD, the streams going in and out of this unit can be added. In HYSYS, streams cannot be added before it has a unit to be attached to.

Specifying Equipment Parameters

In the feed streams in HYSYS it is only necessary to specify two out of the three parameters; temperature, pressure and vapor fraction, in addition to molar/mass flow and composition. HYSYS will calculate the remaining parameters, both upstream and downstream.

A message line at the bottom of each unit window will change color corresponding with the design, as mentioned earlier in this chapter. In addition to the color, HYSYS provides information about the unit status.

In steady state it is possible to make simplifications. For example, instead of adding a heat exchanger, a cooler or heater with a specified energy stream may be used. This could save a lot of time and space in the PFD. If the simulation is going to be transformed into a dynamic model however, some of these simplifications are not feasible.

Running a Simulation

As long as everything is working as it should, the streams and units are given the correct parameters, and HYSYS is able to calculate everything, the simulation is running constantly. If for some reason there is something wrong, a warning message will appear, and the program will automatically stop running. The program will switch from *Solver Active* to *Solver Inactive*, or in the case of dynamic simulation, *Integrator Active* to *Integrator Inactive*.

Report/Results

In HYSYS the entire workbook can be printed out as a report, or if desired, only a specific section. It can for example contain only streams, unit operations, column profiles or heat profiles. Stream and unit operation reports contain all the information that easily can be found while working with the simulation, like conditions for the total stream and each component. Reports for column profiles, for example distillation columns and absorbers, include different parameters. Molar composition and flows of feed and product streams, as well as product recoveries are included. In addition, the column flows, energy, temperature, pressure and composition profiles are included. It is also possible to retrieve a report, which include heat profiles of coolers and heaters. Performance tables in the report include temperature, pressure, heat flow, enthalpy, vapor fraction and so on (Hamid, 2007).

Changing from Steady State to Dynamic Simulation

In HYSYS it is possible to create a dynamic model directly in the *Dynamics* mode just by adding unit operations, or it can be converted from a previously made steady state model. The transition from a steady state to a dynamic model requires some changes. The *Dynamic Assistant* can be used to modify the pressures of the steady state flowsheet. However, these modifications are not always suited for the specific flowsheet, and therefore it is necessary to be critical to the suggestions. When changing a model from steady state to dynamic, more specifications need to be added to the model. It is necessary to ensure that a sensible set of pressure flow specifications is selected. In this way no unrealistic results, such as the flows in the direction of increasing pressure will occur. Hold-ups for the streams to simulate piping and specifications of the unit size should be applied. All unit operations can be sized in the simulation by adding the actual sizes in the plant, or defined sizes. If the equipment sizes are unknown, rules for general equipment sizing can be used. For serious dynamics work, additional changes such as properly configuring control systems, adding extra equipment and so on, needs to be made. Control operations will increase the realism and stability, and disturbances can be modelled using the *Transfer Function* operation. It is also possible to model automated shutdowns and startups by using the *Event Scheduler*, to see how these will affect the process.

It is not necessary to change the fluid package from steady state to dynamics, because HYSYS will simulate the thermal, equilibrium and reactive behavior in a similar way in dynamics as it does in steady state.

Main Difference Between Steady State and Dynamics

In steady state mode the information given by the model is processed as soon as it is supplied. Calculations are performed constantly and these are updated throughout the flowsheet, both upstream and downstream. All balances are considered at the same time, being material, energy and composition balances. Temperature, pressure, flow and composition specifications are considered equally, which means that any parameter can be replaced by another and the software will still be able to solve the model.

In dynamic mode the different balances are not considered at the same time. Material balances for instance are solved at every time step, while energy and composition balances are set to solve less frequently. This is because it would require a lot more capacity to solve for energy and composition balances at every step time. Temperature and composition specifications should be added to every feed stream entering the flowsheet. These specifications are then calculated for each downstream units and streams.

In steady state mode the specifications of the streams are calculated immediately throughout the flowsheet, both upstream and downstream. In dynamic mode however, the integrator must run after placing a unit in the PFD. It is therefore very important to add only one unit operation at a time, and then running the integrator before placing another.

Customizing

In HYSYS it is possible to customize unit operations, property package and kinetic reactions, which then become part of the simulation and function as built in HYSYS object (AspenTech, 2007).

Help

HYSYS is provided with a Help-system where it is possible to search for different topics. It explains what the different tools are used for and how to use them.

Examples/Tutorials

Since HYSYS is widely used, examples and tutorials have been made by AspenTech and professional users. These can easily be accessed on the Internet or found in technical libraries.

6.2 CHEMCAD

CHEMCAD is a software tool used for chemical process simulation, and allows the creation of flowsheets and simulations of various processes. It consists of the following features:

- CC-STEADY STATE
- CC-DYNAMICS
- CC-BATCH
- CC-THERM
- CC-SAFETY NET
- CC-FLASH

CHEMCAD works with the use of licenses, where a license is needed for each of the different features. It is not necessary to have a license for every feature, just the ones that are going to be used (Chemstations, 2007).

CHEMCAD is a relatively cheap simulation software and is for that reason often used by smaller companies or private persons. The prize of a license varies a great deal, depending on what the purpose of the usage is and by whom. Research and development (R&D) companies usually get a 40 % discount of the prize for commercial users. In addition, the price varies with the license duration. Table 14 gives an overview of typical CHEMCAD license prizes.

Table 14 License prizes for CHEMCAD, for unlimited rental and limited hour rental (Lorentz, 2013).

	License prize	
	NOK/year	Total
Unlimited Rental		
1 year	████	████
3 years	████	████
5 years	████	████
Limited Hour Rental		
1 year	████	████
3 years	████	████
5 years	████	████

Starting Up

In CHEMCAD the choice is given, either to create the whole flowsheet at once and then add components afterwards or first add the components and thermodynamics.

Selecting Chemical Components

The components are listed in CHEMCAD's database, which consists of thousands of chemicals. It is possible to search for the wanted chemical, both by name, database ID-number, formula and CAS (Chemical Abstracts Service) number. It is also possible to create customized components and add them to the database for later use.

Choosing chemical components can be executed at any time while creating the simulation, or when the whole flowsheet is finished. However, they need to be added before specifying the stream. In this way, the composition can be added and CHEMCAD can work with the properties of every component.

Selecting Thermodynamics

When adding components for the first time in a new simulation, the *Thermodynamics Wizard* dialog box will appear. The wizard makes general suggestions to fluid package based on the component list and entered parameters for temperature and pressure. It is possible to select components that the wizard should ignore, and this will most likely lead to the wizard suggesting another fluid package. If the user knows the thermodynamic settings, it is also possible to manually select the settings. A local fluid package, which differs from the global fluid package, can be applied to the individual unit operations.

Adding reactions

In CHEMCAD the reactions are added directly to the reactor. It is necessary to know what type of reactions that occur in the process to be able to choose the correct reactor. For example if the reactions are equilibrium reaction, an equilibrium reactor must be chosen. Once the reactor is chosen the reactions can be added. Different reactions need different information, such as stoichiometric coefficients, conversion level, main component and if the reactor is adiabatic or not.

Design/Layout

When starting up, a window appears that includes four subwindows. These include the Workspace, Explorer pane, Palette pane and Message pane. The Workspace is where the actual simulation occurs. The Explorer pane is where each unit operation and stream in the created simulation is found, as well as the thermodynamics. The Palette pane is where all the available units are presented. The Message pane is where errors and warnings are displayed, as well as where personal notes can be written down. The errors and warnings will appear with the oldest one at the top of the list. It is very easy to change the size and shape of all these windows, and they can also be moved around the screen. It is also possible to “pin” and “unpin” the windows. “Pinning” means that a window can be hidden on either side of the Workspace, so that more of the screen can be used for the actual simulation.

Choosing Engineering Units

Before adding any values for the streams and units, it is important to choose the desired engineering units. It is possible to choose a set that is already complete in CHEMCAD, like *English*, *SI* or *metric*, or customize units. If the engineering units are customized, they can be saved and used in a later simulation.

Adding a Stream or Unit

In CHEMCAD it is possible to add streams before placing unit operations in the workspace. When adding the stream, blue and red dots appear on the units, which make it easier to identify where the streams should go in and out.

Specifying Equipment Parameters

The specifications required in a stream are two out of three thermodynamic properties: temperature, pressure and vapor fraction. Before specifying these properties, it is necessary to add the components and a thermodynamic package.

Running a Simulation

After adding the necessary details to the streams and units, the model is ready and it is possible to run the simulation by clicking on the *Run All* button found in the toolbar. CHEMCAD will then calculate material and energy balances throughout the flowsheet, and if there is something

incorrect, warnings and errors will appear on the screen. It is also possible to run one or more unit operations separately, to check if these units give the desired result.

Report/Results

After running the simulation, it is possible to retrieve a number of different results and reports. These can provide data from one stream or unit operation, several units together or the whole flowsheet. If only a few streams are desirable to include in the report, a stream group can be made that includes only these streams. Then it is possible to decide what type of information to include for the streams, whether it is composition or properties, or both. The report can include text or graphical presentations of the desired units. Reports can also include topology, thermodynamics, and mass and energy balances. A text report can be created in either WordPad or Excel, where WordPad is the default in CHEMCAD. If it is more desirable to create a graphical report, CHEMCAD also provides a wide variety of plots.

Changing from Steady State to Dynamic Simulation

In CHEMCAD it is possible to create a dynamic model from the beginning, or it can be transformed from a steady state model. The first thing that needs to be done is switching CHEMCAD from steady state mode to dynamic mode. The software automatically changes the mode to dynamic, which activates different tools that can be used. The next step is to set run time for the simulation, and decide whether the run require a single step or multiple steps. This step size will influence the accuracy of the results the program calculates and also the speed. The highest number of steps possible to specify is 10. When the steps have been specified, selection needs to be done on the streams and units that are going to be recorded.

The simulation is now ready to run. There are three different options for running the simulation: run from initial state, current state or one time interval at a time manually. At any point during the run, it is possible to stop the run. The calculation up to this point can be retrieved, and the simulation can continue by choosing a run command.

Customizing

CHEMCAD opens for customization of templates, components, symbols, unit operations, dialog boxes for unit operation settings and thermophysical rules.

Help

CHEMCAD has a Help-function, which contains information about all the units. It is also possible to search for a specific problem.

Examples/Tutorials

Beginners to CHEMCAD can use the example files that are included in the license. It is also possible to find tutorials and manuals on the Internet or in technical libraries.

6.3 Comparing HYSYS and CHEMCAD

The first thing to take into consideration when choosing simulation software is application and its clientele. As mentioned earlier, HYSYS is more expensive than CHEMCAD, and for this reason their target customers are different. In CHEMCAD it is not necessary to purchase all the available licenses, the user can choose the most suitable for the purpose. Also, the price per year of a license of CHEMCAD will decrease if the customer purchases a license that last for multiple years rather than just a year.

When considering starting up the simulation, there are some differences between HYSYS and CHEMCAD. In HYSYS the components and fluid package needs to be added before building the model. In CHEMCAD however, these things can be added at any point during the simulation or after it has been completed. It is however, also possible to go back and change these things in HYSYS whenever you want. HYSYS just needs these things sorted out before starting, since it calculates parameters in the streams from the start. If the fluid package is changed after the flowsheet has been made, the different properties will be recalculated. If some components are removed or added during or after creating the simulation, this will lead to more work, as the composition of some of the streams must be changed. In addition, if the fluid package is changed to Aspen properties, the composition needs to be re-specified in the feed streams. However, this can be avoided by having the same order of the component lists in HYSYS and Aspen properties databanks.

Reactions are easily added in the SBM in HYSYS and included in a reaction set. From here it is very easy to add them to one or several reactors. In CHEMCAD the reactions have to be added to each reactor. If there is just one reactor in the simulation, neither of the simulation

software have an advantage over the other. If there are several reactors however, it would require less time when using HYSYS.

The designs of the two software are quite different. In HYSYS most of the space is devoted to the PFD where the actual simulation is made. If it is necessary, the Object Palette can be opened and placed wherever on the screen. In CHEMCAD however, the Workspace, Explorer pane, Palette pane and Message pane are all a part of the screen. When creating the simulation, all the units with specifications are easily available. When the simulation is finished, it is possible to remove any of the windows present on the screen. This will lead to a more similar appearance between the software. This section was perceived as better designed in CHEMCAD.

It seems much easier to choose engineering units in CHEMCAD since it is possible to make the changes desired and then use them throughout the work. However, if the parameters are given in different units for different stream, HYSYS could prove to be a better choice since the software allows changing each unit in every stream.

When starting the simulation in HYSYS it is important to remember that the program calculate the properties both upstream and downstream. Thus, it is easy to overspecify the system. It is therefore important to start at one “corner” of the simulation and complete one stream/unit at a time. In CHEMCAD, this is not a problem since the program only calculate downstream. However, the fact that HYSYS calculate both directions is a very large advantage over CHEMCAD. Sometimes when creating a simulation, there are some information missing, and then it will be easier to get that information from HYSYS rather than CHEMCAD. For example if the feed composition is unknown, it is possible to figure this out in HYSYS if the product composition is known.

From a beginner’s point of view, it seems a bit difficult to know what specifications is needed in the different unit operations, in both of the software. The fact that HYSYS always is running makes it somewhat easier, because if something specific is missing a warning message will appear. In CHEMCAD it is necessary to run the simulation to see if there is anything wrong. These messages will appear in the Message Pane, and this makes it more complex. It is easier to see which streams and units that are not working by having signal colors, like in HYSYS.

Running the simulation is much easier in HYSYS than in CHEMCAD since it is possible to run the simulation continuously. In addition, when running the simulation in HYSYS it is possible to open different units, stream or other tools, while in CHEMCAD this is not possible while the simulation is running.

When transforming the model from steady state to dynamics, HYSYS seems to be the best simulation software. The reason for this is that the holdups can be added to the simulation by sizing the units. These numbers are often known, at least if the simulation is based on an actual process. In CHEMCAD however, holdups are included by adding piping or other units. This can be a much more complex approach.

The time consumption for a single run varies a lot within both of the simulation softwares. This is obviously due to the actual size of the simulation, but also the sensitivity. The user can adjust the sensitivity as desired, but it is important to understand that a lower sensitivity will lead to less accurate results.

7. Cost Estimation

Based on the experience obtained from this project, the expected time required to make a training simulator for the formaldehyde plant is two workweeks. This is the estimated time if all values are available and the employee responsible for the model has a great extent of knowledge and experience in HYSYS. The estimated cost for the training simulator is based on the expenses related to the employee after Norwegian standards in addition to the software license. The annual salary of the employee was estimated to 772 000 NOK, which is based on Tekna's wage statistics for civil engineers in the private sector in Norway 01.10.2012 (Tekna, 2012). A license inn HYSYS for commercial usage has an annual cost of approximately [REDACTED] NOK (Pettersen, 2013; Hillestad, 2013). Since the license has an annual fee, it is not an investment, but an operating expense. However, in the calculations the expenses of a license over a five-year period are seen as an investment. The total capital investment of an OTS of the formaldehyde plant was found to [REDACTED] NOK and the calculations are given in Table 15.

Table 15. Calculations of the total investment cost of an OTS by using HYSYS.

	Annual Salary	772 000 NOK
+	Vacation allowance ¹ , 12%	92 640 NOK
=	Employer tax basis	864 640 NOK
+	Employer tax ² , 14.1%	121 914 NOK
=	Annual employee expenses	986 554 NOK
<hr/>		
	Employee expenses, 2 workweeks	37 944 NOK
+	License Aspen HYSYS, 5 years	[REDACTED] NOK
=	Total investment cost	[REDACTED] NOK

^{1,2} (Hoff, 2010)

8. Investments Analysis

This chapter presents the profitability of an OTS built in HYSYS. The investment analysis includes comparing the profit of an OTS made in HYSYS to operations of the factory without OTS as well as an OTS made with CHEMCAD simulation software. To be able to do this investment analysis a cost estimation of the formaldehyde plant and the CHEMCAD simulation software is necessary.

8.1 Cost and Investment Analysis of the Formaldehyde Plant

It was assumed that installation of the main equipment in the Perstorp formaldehyde plant has a total cost of ██████ USD. The main equipment of the plant are the reactor, absorber, recirculation blowers, HTF-condenser, prevaporizer and vaporizer (Pajalic, 2013a). The total cost of the equipment was multiplied with a Lang factor of 5.0 to achieve the total investment cost of the entire plant. The total investment cost were calculated to ██████ NOK, see Table 16.

Table 16. Total plant investment.

	Installation of main components ¹	██████	NOK
*	Lang factor ²	5.0	
=	Total plant investment	██████	NOK

¹ Calculated from USD to NOK with a factor of 5.72 (Nordea, n.d.).

² (Lang, 1948)

It was assumed that the formaldehyde plant produces 50 000 tons of formalin per year, with a formaldehyde content of 50% (Pajalic, 2013b). The expected down-pay time of this specific plant was five years and the net present value of the plant was assumed to be 0 NOK. In other words, the sum of the cash flow (included interests) over these five years is equal to the plant investment.

Table 17 shows the calculation of the daily cash flow.

Table 17. Calculation of daily cash flow.

	Installation of entire plant	████████	NOK
÷	Down-pay time	5	Years
÷	Days of operating	365	Days/year
=	Cash flow per day	████████	NOK/day

The time intervals between every plant turnover and start-up/shut-down increases with the use of OTS. It was expected that the formaldehyde plant could reduce the number of days with operation stops by ten over a five-year period. This would provide the company with about ████████ NOK to invest in the OTS. The calculations are shown in Table 18. If the investments of the OTS exceeds this amount, the investment will not be profitable.

Table 18. Cash available for investment in OTS.

	Cash flow per day	████████	NOK/day
*	Number of reduced stops	10	Stops/5 years
=	Cash available for investment in OTS	████████	NOK

8.2 Cost Estimation of a OTS made with CHEMCAD Simulation Software

A license inn CHEMCAD for commercial usage, with a five year agreement, has an annual cost of ████████ NOK (Lorentz, 2013). The total investment cost for an OTS made in CHEMCAD are presented in Table 19. Annual employee expenses, shown in Table 15, and the required time for creating the OTS, are assumed equal for HYSYS and CHEMCAD.

Table 19. Calculations of the total investment cost of an OTS by using CHEMCAD.

	Employee expenses, 2 workweeks	37 944	NOK
+	License CHEMCAD, 5 years	████████	NOK
=	Total investment cost	████████	NOK

8.3 Investment Analysis of HYSYS OTS

The calculation of the profitability of an OTS in HYSYS was based on the calculated cash available for investment in OTS as well as the OTS investment cost. The Table 20 shows the results from the calculations. The investment will give an expense of approximately 68 000 NOK, in other words the investment is not profitable.

Table 20. Profit of the investment of OTS made with HYSYS.

	Cash available for investment in OTS	██████	NOK
-	OTS investment cost	██████	NOK
=	Profit of investment	-67 804	NOK

The same calculations were made for the investment of an OTS in CHEMCAD, the results are given in Table 21. The investment analysis shows that the company would save approximately 126 000 NOK by using CHEMCAD OTS.

Table 21. Profit of the investment of OTS made with CHEMCAD.

	Cash available for investment in OTS	██████	NOK
-	OTS investment cost	██████	NOK
=	Profit of investment	126 176	NOK

Comparing OTS made in HYSYS and CHEMCAD shows that using CHEMCAD will give a higher profit of almost 200 000 NOK compared to HYSYS.

9. Discussion

A steady state model of Perstorp factory five was built in HYSYS Aspen. The model was design on the basis of a CHEMCAD model of the process, provided by Perstorp.

The reactor was modelled as one kinetic plug flow reactor. Instead of applying the HTF as a cooling medium to the reactor, the outlet temperature was specified. If a dynamic model were to be made, the cycle of the HTF in the condenser needs to be included. When modelling the reactor in HYSYS the specified kinetics had to be manually adjusted to obtain similar result as the CHEMCAD reference values. The tuning was preformed according to the steady state values, but also at different total mass flow rates in the feed stream. The result of the simulations of the reactor showed that when adjusting the total flow rate into the reactor, the product flow rate of the components followed the same trend as the reference values. The flow rate of methanol and carbon monoxide did not correspond to the reference values to the same extend as the other components. At a total flow rate of 30 000 kg/h into the reactor the product flow rate of carbon monoxide had a deviation of 25.3%, while the peak of deviation for the flow of methanol was at a feed flow rate of 60 000 kg/h, where the deviation was 13.2%. The stimulations were performed at a total inlet flow between 30 000 - 60 000 kg/h. Thus, the deviation would increase even more when the flow rate distanced itself from the steady state values.

The Formaldehyde-Methanol-Water system is highly non-ideal, which made it very difficult to find a suitable thermodynamic model. Several different fluid packages were tested, and NRTL was chosen, even though deviations from the reference CHEMCAD values were observed in the streams connected to the absorber. To obtain a product within the same range as the reference values, some specifications were adjusted. Consequently, some of the streams in the model were not specified equal to the CHEMCAD reference values. If a more exact model or a dynamic model were to be made, it would be necessary to make a customized fluid package for this process. Thus, the specifications throughout the model would be more correct. One of the adjustments was the addition of a methanol makeup flow. Methanol is used commercially to stabilize formaldehyde. After adjustments were made, the product specifications had small deviation from the CHEMCAD reference values. The main components in the product stream, water, formaldehyde and methanol, established the following weight percent: 51.8%, 47.9%

and 0.29%, and the total product flow rate was 8923 kg/h. These values had less than 0.2% deviation from the CHEMCAD reference values.

Mass and energy balances were set up for the whole process, the reactor and the absorber. The balances summed to zero, which pointed to correct calculation with conserved mass and energy. The mass and energy balances developed from the HYSYS model, were compared to equivalent balances from the CHEMCAD model. Large deviations were observed. However, this was expected to be a consequence of the adjustment while tuning the HYSYS model.

HYSYS and CHEMCAD simulation software were compared with respect to usability, design and costs. There are a lot of similarities in HYSYS and CHEMCAD, when thinking about how to insert thermodynamics, reactions, components, units and streams. In both software, these things are relatively easy to understand and execute. From a beginners point of view CHEMCAD seems to be easier to understand in terms of design of the Workspace, Explorer pane, Palette pane and Message pane. In addition, the thermodynamic wizard helps the user in deciding the correct fluid package more in CHEMCAD than in HYSYS. It is however important to remember that the wizard only gives a suggestion that the user needs to be critical about.

The design of the program is easier to understand in HYSYS, since it has color codes on streams and units. If a unit or stream is not working, this will be detected immediately since the simulation is running continuously as long as everything is ok. In CHEMCAD it is more difficult to know when something is not working before the simulation is run.

When modeling the process in HYSYS it was easy to add local thermodynamic fluid package to one specific unit. In CHEMCAD however, this was more complex, and not as easy to understand. In addition, when a window was opened in CHEMCAD it seemed impossible to open another window simultaneously. When building a model in CHEMCAD this was seen as a disadvantage. In HYSYS it was very easy to open several windows at the same time. This, as well as spreadsheets, were found to be very useful when tuning the model to achieve the desired product. In HYSYS it was also possible to open other windows while the simulation was running. This seemed impossible to do in CHEMCAD, consequently nothing could be done during a run.

From a new users point of view, it is difficult to compare the software on an advanced level. HYSYS seemed to be design to operate petroleum products better than CHEMCAD, but CHEMCAD might have an advantage in chemical processes. However, it is possible to customize fluid packages and in this way, more reliable results may be obtained in HYSYS. When customizing the thermodynamics, it is expected that various plant data are required to fit binary parameters, in addition to good knowledge of the software. When building an OTS, HYSYS seems to be the best choice. In HYSYS it is possible to design units to meet certain requirements and specifications. In CHAMCAD this seems to be more difficult, where detours and more units are used.

The economic perspective of using OTS was looked into. It was expected that the formaldehyde plant could reduce the number of days with operation stops by ten over a five-year period if they used an OTS. The profit of using an OTS made in HYSYS were calculated, and the result showed an expense of approximately 68 000 NOK. Thus, the investment of the OTS was not profitable. In the calculations, several assumptions were made. Consequently, the calculations are estimations and have a high degree of uncertainty. The price of the license is negotiable, and as a consequence it is difficult to get an exact number of the price. The expense of the license was based on prices for commercial usage. It is reasonable to assume that industrial usage and contracts for a longer period of time will lead to a decrease in the price. It is also a high possibility that one custom made OTS can be used for several factories with few adjustments. Therefore, even though the investment analysis pointed to a negative profit by using simulation models, it is likely that this is misleading and that companies can have economic benefits from the models.

If an equivalent OTS were built in CHEMCAD instead of HYSYS, the total investment cost of the OTS would drop, since the license in CHEMCAD is cheaper than HYSYS. The profit of using an OTS made in CHEMCAD were calculated to approximately 126 000 NOK. However, which software is best suited for the task, can be discussed.

Even though the focus has been on the economical aspect of the use of simulation models, it is important to empathize other benefits. Engineers and operators needs to understand and have knowledge about the process design and the control system, as well as the normal and abnormal activities. To manage the engineering of these processes and systems with increasing size and complexity, the engineers needs training. Learning by doing and learning based on experience

and experiments is a critical way to develop the competence of engineers and operators. According to Roe, et al (2010) half of the errors and serious incidents caused by humans can be avoided when using simulators when training the engineers and operators.

10. Conclusion

This experience shows how fundamental the understanding of thermodynamics is in the development of simulation models. From a beginner's perspective, CHEMCAD seems to be the better choice when it comes to the Formox process, because it already contains suitable fluid packages and are economically beneficial. HYSYS requires a higher knowledge base, since these specific fluid packages needs to be customized. However, HYSYS appear to be the better software for process simulation in general, especially when looking at usability.

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**Appendix A. P&IDs of the Perstorp Formaldehyde Factory
Number 5**

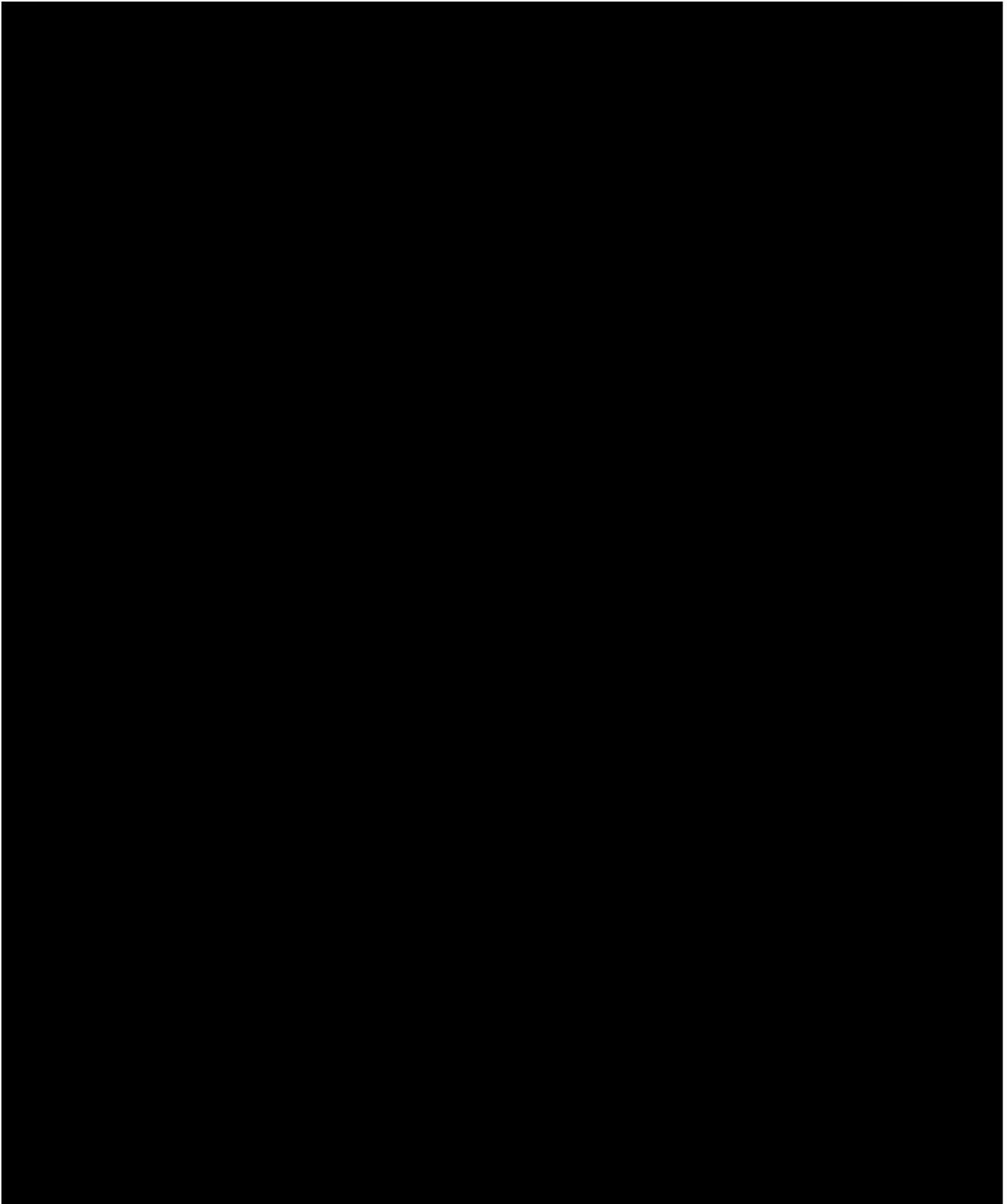


Figure A1. P&ID of the absorber in Perstorp's formaldehyde factory number 5.

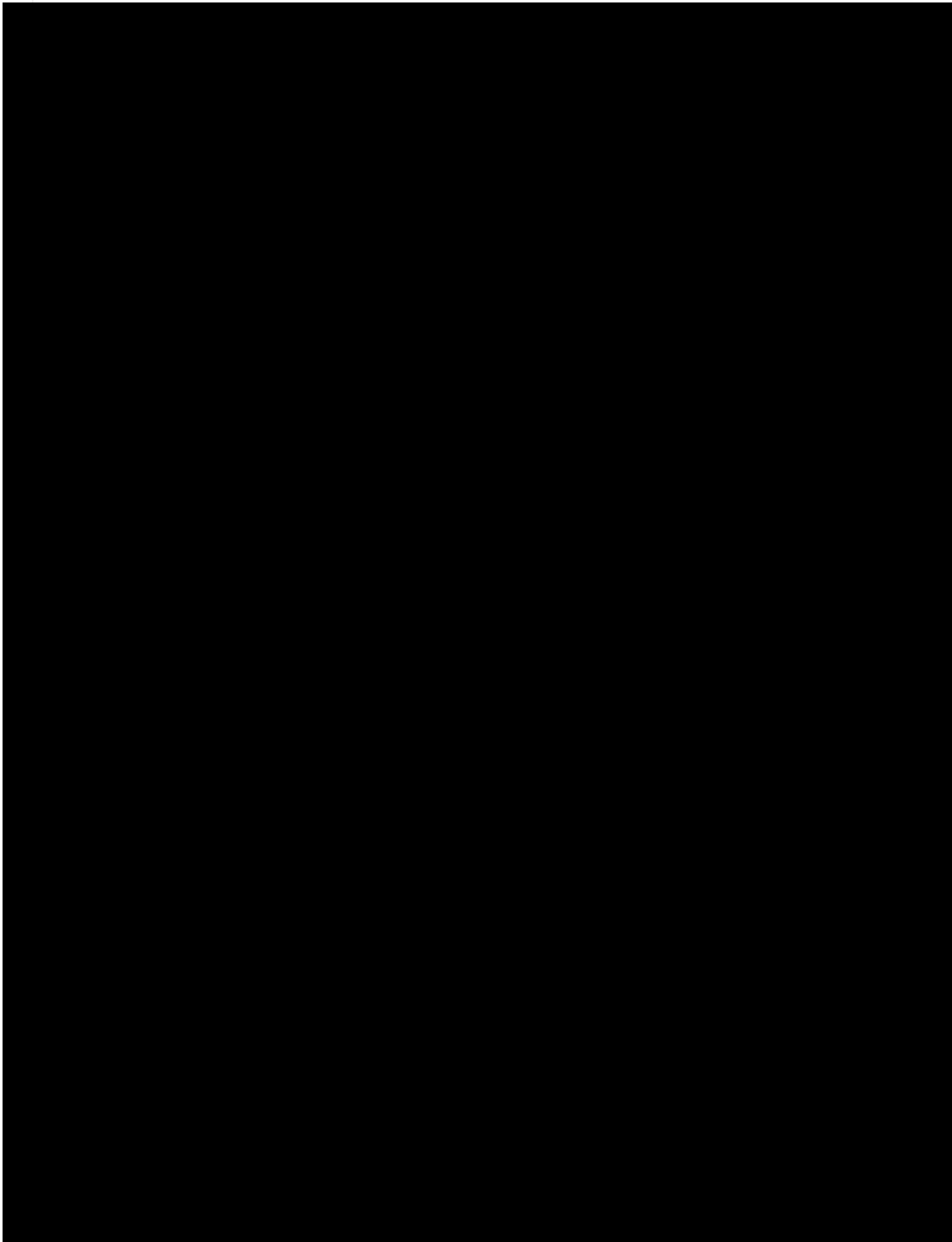


Figure A2. P&ID of the reactor system in Perstorp's formaldehyde factory number 5.

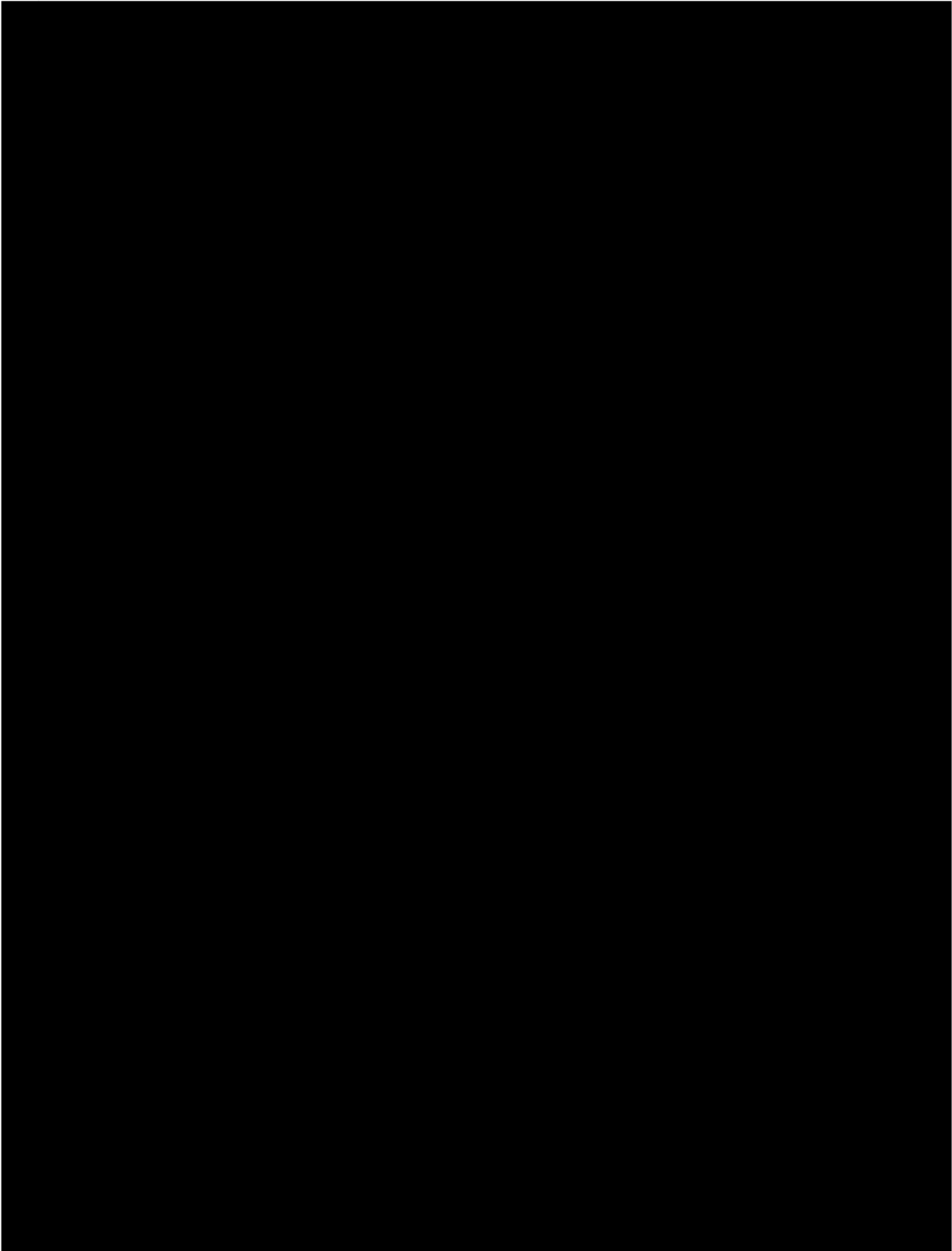


Figure A3. P&ID of the pump system in Perstorp's formaldehyde factory number 5.

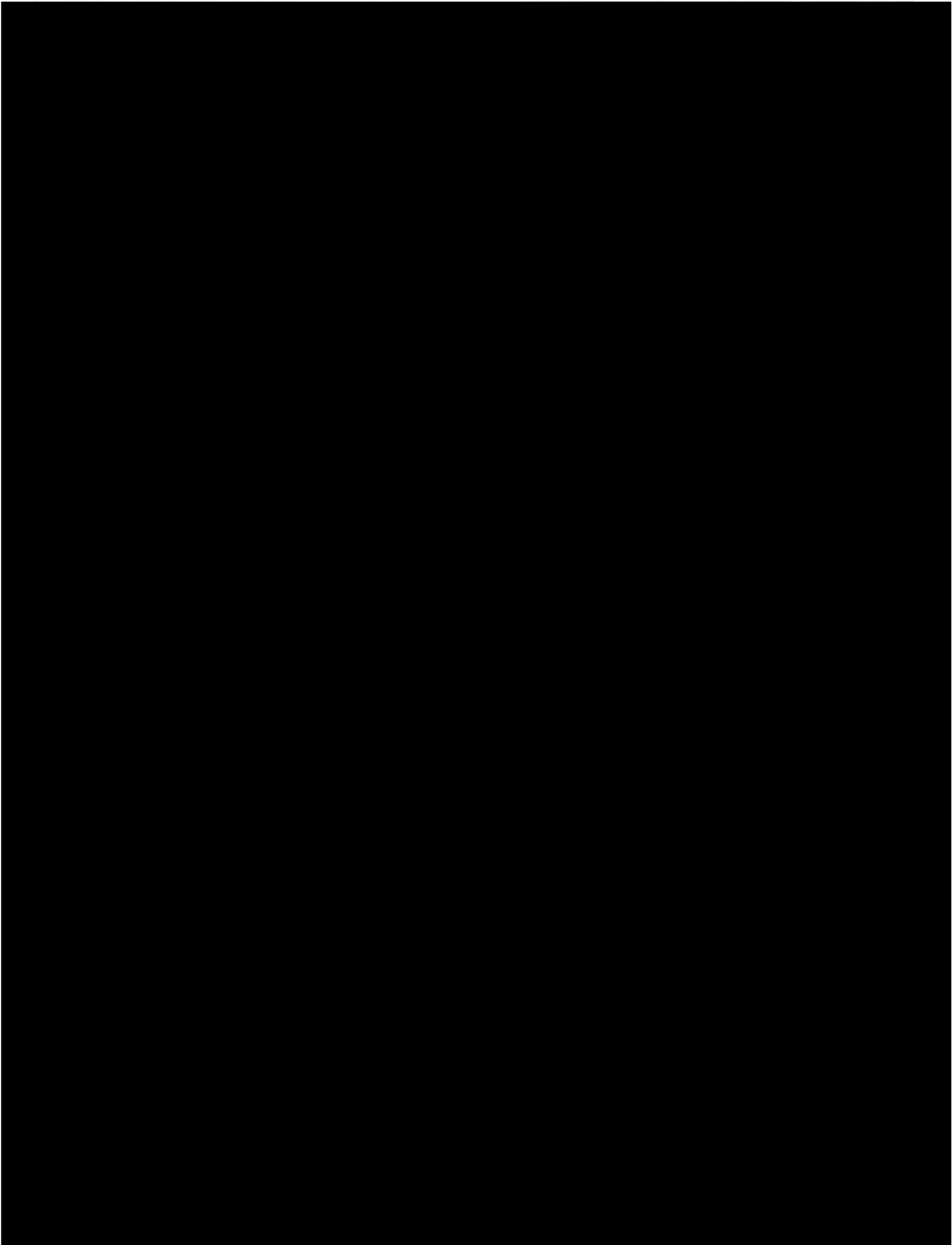


Figure A4. P&ID of the residual gas combustion in Perstorp's formaldehyde factory number 5.

Appendix B. Thermodynamic Models in HYSYS

This appendix presents the results of different thermodynamics models in HYSYS. Several fluid packages were applied to a model containing two unit operations in HYSYS. The results were compared to reference values obtained from a CHEMCAD model with Maurer fluid package. Table B1 to B9 present the results from simulations in HYSYS, the deviations from the reference values is also included. Where the absorber did not converge, NC is written.

Table B1. Specifications of outlet flows [61] and [66] from absorber and [83] and [55] from tank, when HYSYS with Wilson fluid package is used. In addition, the deviation from reference values (CHEMCAD values).

Outlet Flows	HYSYS, Wilson			
	[61]	[66]	[83]	[55]
Total flow [kg/h]	NC	NC	38186	3580
Water flow [kg/h]	NC	NC	83.7	3501.0
Methanol flow [kg/h]	NC	NC	23.1	27.3
Formaldehyde flow [kg/h]	NC	NC	0.00	51.3
Temperature [°C]	NC	NC	29.9	29.9
Pressure [bar]	NC	NC	1.31	1.31
Δ Total flow [kg/h]	-	-	-762.3	760.8
Δ Water flow [kg/h]	-	-	-742.4	743.8
Δ Methanol flow [kg/h]	-	-	-15.8	14.9
Δ Formaldehyde flow [kg/h]	-	-	-7.50	6.05
Δ Temperature [°C]	-	-	0.00	0.00
Δ Pressure [bar]	-	-	0.05	0.05

Table B2. Specifications of outlet flows [61] and [66] from absorber and [83] and [55] from tank, when HYSYS with UNIQUAC fluid package is used. In addition, the deviation from reference values (CHEMCAD values).

	HYSYS, UNIQUAC			
Outlet Flows	[61]	[66]	[83]	[55]
Total flow [kg/h]	NC	NC	3224	38542
Water flow [kg/h]	NC	NC	3143	442
Methanol flow [kg/h]	NC	NC	30.3	20.1
Formaldehyde flow [kg/h]	NC	NC	51.3	0.0
Temperature [°C]	NC	NC	29.9	29.9
Pressure [bar]	NC	NC	1.31	1.31
Δ Total flow [kg/h]	-	-	-35724	35723
Δ Water flow [kg/h]	-	-	2316	-2315
Δ Methanol flow [kg/h]	-	-	-8.58	7.68
Δ Formaldehyde flow [kg/h]	-	-	43.8	-45.3
Δ Temperature [°C]	-	-	0.00	0.00
Δ Pressure [bar]	-	-	0.05	0.05

Table B3. Specifications of outlet flows [61] and [66] from absorber and [83] and [55] from tank, when HYSYS with NRTL (aspen properties) fluid package is used. In addition, the deviation from reference values (CHEMCAD values).

	HYSYS, NRTL (Aspen Properties)			
Outlet Flows	[61]	[66]	[83]	[55]
Total flow [kg/h]	49915	8294	38960	2807
Water flow [kg/h]	5365	8142	802	2783
Methanol flow [kg/h]	74.9	21.7	36.2	14.1
Formaldehyde flow [kg/h]	6399	115	49.9	1.40
Temperature [°C]	62.3	63.2	29.9	29.9
Pressure [bar]	1.36	1.41	1.31	1.31
Δ Total flow [kg/h]	563	-631	11.1	-12.6
Δ Water flow [kg/h]	-3579	3521	-24.0	25.4
Δ Methanol flow [kg/h]	4.43	-3.75	-2.66	1.76
Δ Formaldehyde flow [kg/h]	4145	-4156	42.4	-43.9
Δ Temperature [°C]	-14.3	-14.6	0.00	0.00
Δ Pressure [bar]	0.00	0.00	0.05	0.05

Table B4. Specifications of outlet flows [61] and [66] from absorber and [83] and [55] from tank, when HYSYS with NRTL-HOC (aspen properties) fluid package is used. In addition, the deviation from reference values (CHEMCAD values).

	HYSYS, NRTL-HOC (Aspen Properties)			
Outlet Flows	[61]	[66]	[83]	[55]
Total flow [kg/h]	49726	8483	38948	2818
Water flow [kg/h]	5232	8276	805	2780
Methanol flow [kg/h]	72.4	24.1	35.9	14.4
Formaldehyde flow [kg/h]	6368	146	49.8	1.57
Temperature [°C]	61.7	63.0	29.9	29.9
Pressure [bar]	1.36	1.41	1.31	1.31
Δ Total flow [kg/h]	373	-441	-0.6	-0.9
Δ Water flow [kg/h]	-3713	3655	-21.1	22.4
Δ Methanol flow [kg/h]	2.0	-1.3	-2.96	2.06
Δ Formaldehyde flow [kg/h]	4115	-4126	42.3	-43.7
Δ Temperature [°C]	-14.9	-14.7	0.00	0.00
Δ Pressure [bar]	0.00	0.00	0.05	0.05

Table B5. Specifications of outlet flows [61] and [66] from absorber and [83] and [55] from tank, when HYSYS with UNIFAC (aspen properties) fluid package is used. In addition, the deviation from reference values (CHEMCAD values).

	HYSYS, UNIFAC (Aspen Properties)			
Outlet Flows	[61]	[66]	[83]	[55]
Total flow [kg/h]	50150	8059	38970	2797
Water flow [kg/h]	5538	7969	810	2775
Methanol flow [kg/h]	85.2	11.3	38.7	11.6
Formaldehyde flow [kg/h]	6448	65.7	50.6	0.72
Temperature [°C]	62.6	63.0	29.9	29.9
Pressure [bar]	1.36	1.41	1.31	1.31
Δ Total flow [kg/h]	797	-866	21.1	-22.6
Δ Water flow [kg/h]	-3406	3348	-16.1	17.5
Δ Methanol flow [kg/h]	14.8	-14.1	-0.14	-0.76
Δ Formaldehyde flow [kg/h]	4195	-4206	43.1	-44.6
Δ Temperature [°C]	-14.0	-14.7	0.00	0.00
Δ Pressure [bar]	0.00	0.00	0.05	0.05

Table B6. Specifications of outlet flows [61] and [66] from absorber and [83] and [55] from tank, when HYSYS with UNIFAC-HOC (aspen properties) fluid package is used. In addition, the deviation from reference values (CHEMCAD values).

	HYSYS, UNIFAC-HOC (Aspen Properties)			
Outlet Flows	[61]	[66]	[83]	[55]
Total flow [kg/h]	50117	8092	38961	2805
Water flow [kg/h]	5522	7986	807	2778
Methanol flow [kg/h]	84.9	11.6	38.5	11.8
Formaldehyde flow [kg/h]	6444	69.6	50.6	0.75
Temperature [°C]	62.5	63.0	29.9	29.9
Pressure [bar]	1.36	1.41	1.31	1.31
Δ Total flow [kg/h]	765	-833	12.8	-14.3
Δ Water flow [kg/h]	-3423	3365	-19.0	20.4
Δ Methanol flow [kg/h]	14.5	-13.8	-0.33	-0.57
Δ Formaldehyde flow [kg/h]	4191	-4202	43.1	-44.5
Δ Temperature [°C]	-14.1	-14.7	0.00	0.00
Δ Pressure [bar]	0.00	0.00	0.05	0.05

Table B7. Specifications of outlet flows [61] and [66] from absorber and [83] and [55] from tank, when HYSYS with PSRK (aspen properties) fluid package is used. In addition, the deviation from reference values (CHEMCAD values).

	HYSYS, PSRK (Aspen Properties)			
Outlet Flows	[61]	[66]	[83]	[55]
Total flow [kg/h]	NC	NC	38990	2776
Water flow [kg/h]	NC	NC	821	2764
Methanol flow [kg/h]	NC	NC	38.8	11.5
Formaldehyde flow [kg/h]	NC	NC	50.8	0.55
Temperature [°C]	NC	NC	29.9	29.9
Pressure [bar]	NC	NC	1.31	1.31
Δ Total flow [kg/h]	-	-	41.7	-43.3
Δ Water flow [kg/h]	-	-	-5.11	6.50
Δ Methanol flow [kg/h]	-	-	-0.04	-0.86
Δ Formaldehyde flow [kg/h]	-	-	43.3	-44.7
Δ Temperature [°C]	-	-	0.00	0.00
Δ Pressure [bar]	-	-	0.05	0.05

Table B8. Specifications of outlet flows [61] and [66] from absorber and [83] and [55] from tank, when HYSYS with Wilson (aspen properties) fluid package is used. In addition, the deviation from reference values (CHEMCAD values).

	HYSYS, Wilson (Aspen Properties)			
Outlet Flows	[61]	[66]	[83]	[55]
Total flow [kg/h]	NC	NC	38957	2809
Water flow [kg/h]	NC	NC	802	2783
Methanol flow [kg/h]	NC	NC	35.3	15.1
Formaldehyde flow [kg/h]	NC	NC	48.6	2.70
Temperature [°C]	NC	NC	29.9	29.9
Pressure [bar]	NC	NC	1.31	1.31
Δ Total flow [kg/h]	-	-	8.69	-10.2
Δ Water flow [kg/h]	-	-	-24.2	25.5
Δ Methanol flow [kg/h]	-	-	-3.58	2.68
Δ Formaldehyde flow [kg/h]	-	-	41.1	-42.6
Δ Temperature [°C]	-	-	0.00	0.00
Δ Pressure [bar]	-	-	0.05	0.05

Table B9. Specifications of outlet flows [61] and [66] from absorber and [83] and [55] from tank, when HYSYS with UNIQUAC (aspen properties) fluid package is used. In addition, the deviation from reference values (CHEMCAD values).

	HYSYS, UNIQUAC (Aspen Properties)			
Outlet Flows	[61]	[66]	[83]	[55]
Total flow [kg/h]	NC	NC	38965	2802
Water flow [kg/h]	NC	NC	803	2782
Methanol flow [kg/h]	NC	NC	36.2	14.1
Formaldehyde flow [kg/h]	NC	NC	50.2	1.10
Temperature [°C]	NC	NC	29.9	29.9
Pressure [bar]	NC	NC	1.31	1.31
Δ Total flow [kg/h]	-	-	15.9	-17.4
Δ Water flow [kg/h]	-	-	-23.2	24.6
Δ Methanol flow [kg/h]	-	-	-2.62	1.72
Δ Formaldehyde flow [kg/h]	-	-	42.7	-44.2
Δ Temperature [°C]	-	-	0.00	0.00
Δ Pressure [bar]	-	-	0.05	0.05

Appendix C. Specifications of Reaction Kinetics in CHEMCAD and HYSYS

This appendix present the specifications of the reaction kinetics applied to the reactor in Perstorps CHEMCAD model and in the HYSYS model. The kinetics specified in the CHEMCAD model is given in Table C1. The kinetics specified in the HYSYS model is given in Figure C1, C2, and C3, for reaction (1), (3) and (4), respectively.

Table C1. Specifications of the kinetics for all three reactions in the ten reactors in the CHEMCAD model.

Reactor	63	64	65	66	67	68	69	70	71	72
Number of reactions	3	3	3	3	3	3	3	3	3	3
Reaction 1										
Frequency factor (A)	0.05	0.5	0.5	0.53	0.65	0.895	1	1	1	0.65
Activation Energy (E)	0	0	0	0	0	0	0	0	0	0
Beta Factor (β)	1	1	1	1	1	1	0.95	0.9	0.85	0.6
Reaction 2										
Frequency factor (A)	0.01	0.1	0.1	0.106	0.13	0.179	0.2	0.2	0.2	0.13
Activation Energy (E)	0	0	0	0	0	0	0	0	0	0
Beta Factor (β)	1	1	1	1	1	1	0.95	0.9	0.85	0.6
Reaction 3										
Frequency factor (A)	0.05	0.5	0.5	0.53	0.65	0.895	1	1	1	0.65
Activation Energy (E)	0	0	0	0	0	0	0	0	0	0
Beta Factor (β)	1	1	1	1	1	1	0.95	0.9	0.85	0.6

Kinetic: Rxn-1

STOICHIOMETRY

Component	Molecular Weight	Stoich Coeff	Forward Order	Reverse Order
Methanol	32.04	-2 *	7.600e-002 *	0.0000 *
Oxygen	32.00	-1 *	1.000 *	0.0000 *
Formaldehyde	30.03	2 *	0.0000 *	2.000 *
H2O	18.02	2 *	0.0000 *	2.000 *

Balance Error : 0.0000

Reaction Heat (25 C) : -1.565e+005 kJ/kgmole

BASIS

Basis	Base Component	Rxn Phase	Min. Temp (C)	Max. Temp (C)
Partial Pres	Methanol	VapourPhase	-273.1	3000

PARAMETERS

Forward Reaction		Reverse Reaction	
A :	1.960e+006 *	A :	---
E :	9.800e+004 *	E :	---

Figure C1. Specifications of kinetics in reaction (1), report from HYSYS.

Kinetic: Rxn-2

STOICHIOMETRY

Component	Molecular Weight	Stoich Coeff	Forward Order	Reverse Order
Formaldehyde	30.03	-2 *	2.000	0.0000
Oxygen	32.00	-1 *	1.000	0.0000
CO	28.01	2 *	0.0000	2.000
H2O	18.02	2 *	0.0000	2.000

Balance Error : 0.0000

Reaction Heat (25 C) : -2.364e+005 kJ/kgmole

BASIS

Basis	Base Component	Rxn Phase	Min. Temp (C)	Max. Temp (C)
Partial Pres	Formaldehyde	VapourPhase	-273.1	3000

PARAMETERS

Forward Reaction	Reverse Reaction
A : 5.300e-006	A' : ---
E : 1.100e+004	E' : ---

Figure C2. Specifications of kinetics in reaction (3), report from HYSYS.

Kinetic: Rxn-3

STOICHIOMETRY

Component	Molecular Weight	Stoich Coeff	Forward Order	Reverse Order
Methanol	32.04	-2 *	2.000	0.0000
dim-Ether	46.07	1 *	0.0000	1.000
H2O	18.02	1 *	0.0000	1.000

Balance Error : 0.0000

Reaction Heat (25 C) : -1.171e+004 kJ/kgmole

BASIS

Basis	Base Component	Rxn Phase	Min. Temp (C)	Max. Temp (C)
Partial Pres	Methanol	VapourPhase	-273.1	3000

PARAMETERS

Forward Reaction	Reverse Reaction
A : 6500	A' : ---
E : 9.800e+004	E' : ---

Figure C3. Specifications of kinetics in reaction (4), report from HYSYS.

Appendix D. Modelling the Absorber

The thermodynamics in the absorber did not correspond well to the CHEMCAD reference values. Some flows in the HYSYS model were modified to give the desired product composition and flow rate. The values modified is given in Table D1.

Table D1. Modified flows, reference values from CHEMCAD and new values from HYSYS

Adjusted variable	Flow	Reference values	New values
		CHEMCAD	HYSYS
Temperature [°C]	[83]	29.9	13
Temperature [°C]	[51]	41.9	20
Temperature [°C]	[53]	60.0	55
Temperature [°C]	[36]	52.2	40
Temperature [°C]	[23]	146	143
Total mass flow [kg/h]	[45]	2030	1850
Total mass flow [kg/h]	[127]	26981	29000
Total mass flow [kg/h]	B Methanol makeup	0	26

Appendix E. Complex Steady State Model

The outline of a complex steady state model was made. This was developed more similar to the CHEMCAD model, and some parts of this model could be useful when building a dynamic model.

The prevaporizer (E-3), the vaporizer (E-1), the steam generator (E-7) and the heat exchanger (E-30), were all modelled as heat exchangers in a similar manner as in the CHEMCAD model. In this model the water cooling system is also included. Figure E1 shows the model made in HYSYS. All the specifications were set equal to the CHEMCAD model. This model is not tuned, thus, the results is not accurate.

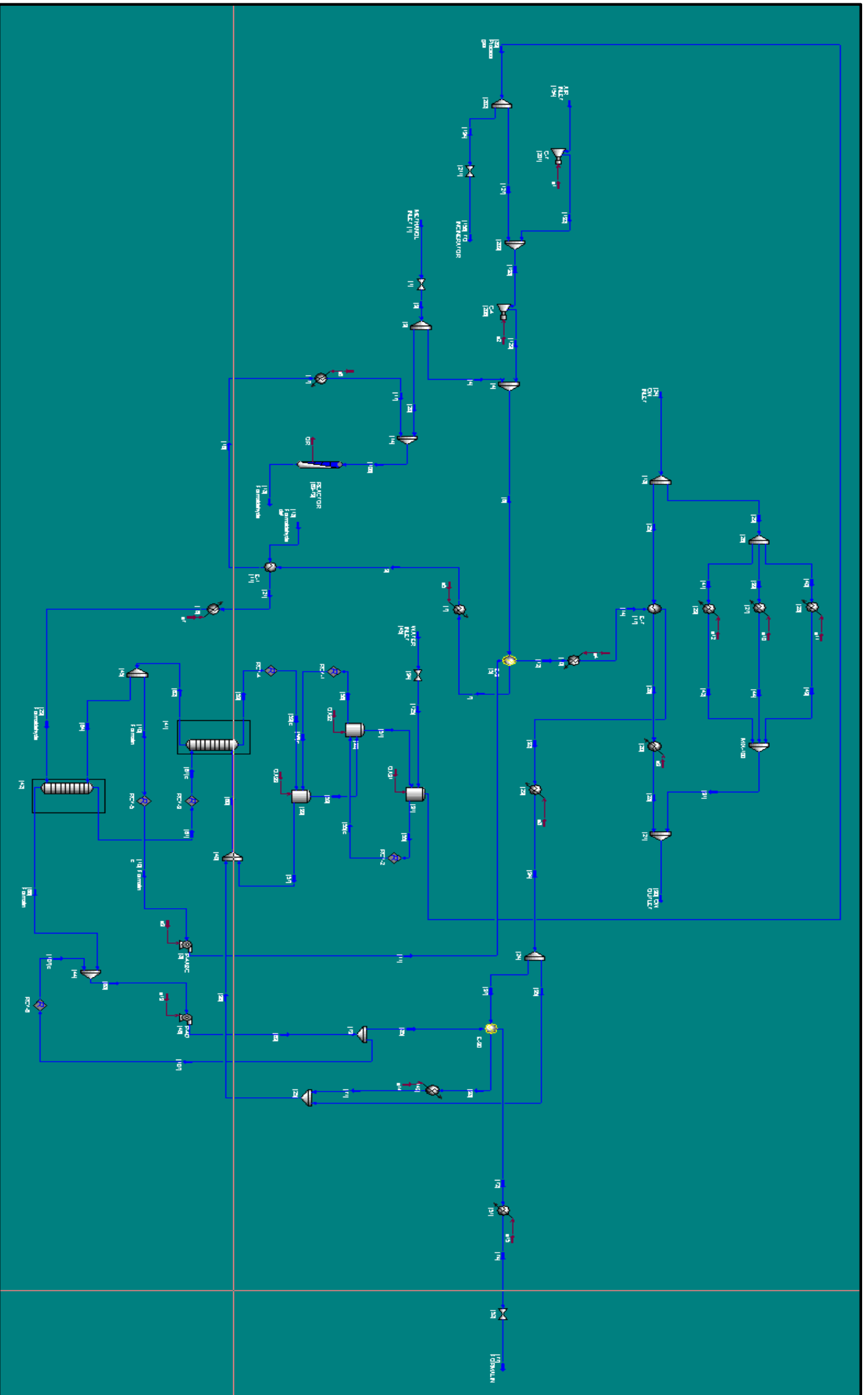


Figure E1. An outline of a complex steady state model of the formaldehyde process in HYSYS.

Appendix F. Mass Balance of Unit Operations in the Absorber

Table F1 to F5 contains the mass balances of five unit operations in the absorber. The mass balances sums to zero for all the unit operations in both software. The difference between CHEMCAD values and HYSYS values are relatively large. This is due to different thermodynamics as well as different specifications.

Table F1. Mass balance of the lower absorber.

Lower Absorber [42] Mass Balance				
Components [kg/h]	Inlet streams		Outlet streams	
	[64]	[23] Form.hyde	[61]	[66] Formalin
CHEMCAD				
H2O	10147	3419	8944	4621
O2	0.014	2537	2537	0.008
Methanol	31.9	64.0	70.4	25.4
diM-Ether	8.11	152	154	6.78
Formaldehyde	2247	4278	2254	4271
CO	0.002	514	514	0.001
N2	0.10	34251	34251	0.062
CO2	0.002	27.5	27.5	0.001
Argon	0.005	601	601	0.003
Total	12434	45844	49353	8925
HYSYS				
H2O	6314	3058	4755	4618
O2	0.06	2678	2678	0.07
Methanol	1.18	76.6	77.5	0.26
diM-Ether	5.09	167	168	3.15
Formaldehyde	3822	4344	3891	4275
CO	0.01	525	525	0.01
N2	0.59	36355	36355	0.76
CO2	0.01	29.2	29.2	0.01
Argon	0.02	638	638	0.02
Total	10143	47871	49117	8897
<i>Deviation</i>	<i>2291</i>	<i>-2027</i>	<i>236</i>	<i>28</i>

Table F2. Mass balance of the upper absorber.

Upper Absorber [41] Mass Balance				
Components [kg/h]	Inlet streams		Outlet streams	
	[60]	[61]	[59]	[62]
CHEMCAD				
H2O	97340	8944	4453	101830
O2	0.13	2537	2537	0.14
Methanol	305	70.4	55.4	320
diM-Ether	78.3	154	151	81.4
Formaldehyde	20898	2254	605	22547
CO	0.02	514	514	0.02
N2	1.00	34251	34251	1.04
CO2	0.02	27.5	27.5	0.02
Argon	0.05	601	601	0.05
Total	118623	49353	43195	124780
HYSYS				
H2O	73491	4755	1997	76248
O2	0.65	2678	2678	0.68
Methanol	14.5	77.5	77.8	14.3
diM-Ether	59.1	169	166	61.5
Formaldehyde	43829	3891	1562	46158
CO	0.11	525	525	0.12
N2	6.72	36355	36355	7.10
CO2	0.12	29.2	29.2	0.13
Argon	0.19	638	638	0.20
Total	117401	49117	44028	122490
<i>Deviation</i>	<i>1222</i>	<i>236</i>	<i>-833</i>	<i>2290</i>

Table F3. Mass balance of the lower tank.

Lower Tank [33] Mass Balance				
Components [kg/h]	Inlet streams		Outlet streams	
	[56]'	[59]'	[53]	[57]
CHEMCAD				
H2O	5122	4453	3918	5657
O2	0.01	2537	2537	0.01
Methanol	22.4	55.4	61.3	16.6
diM-Ether	6.72	151	152	4.98
Formaldehyde	292	605	299	598
CO	0.002	514	514	0.001
N2	0.07	34251	34251	0.07
CO2	0.002	27.5	27.5	0.001
Argon	0.003	601	601	0.003
Total	5443	43195	42362	6275
HYSYS				
H2O	4553	1997	2994	3556
O2	0.03	2678	2678	0.02
Methanol	5.83	77.8	82.2	1.47
diM-Ether	9.04	166	173	2.67
Formaldehyde	1546	1562	1614	1494
CO	0.01	525	525	0.003
N2	0.29	36355	36355	0.20
CO2	0.01	29.2	29.2	0.004
Argon	0.01	638	638	0.006
Total	6114	44028	45088	5054
<i>Deviation</i>	<i>-671</i>	<i>-833</i>	<i>-2726</i>	<i>1221</i>

Table F4. Mass balance of the middle tank.

Middle Tank [32] Mass Balance				
Components [kg/h]	Inlet streams		Outlet streams	
	[53]	[55]'	[51]	[56]
CHEMCAD				
H2O	3918	2757	1553	5122
O2	2537	0.007	2537	0.01
Methanol	61.3	12.4	51.2	22.4
diM-Ether	152	4.46	150	6.72
Formaldehyde	299	45.3	52.8	292
CO	514	0.001	514	0.002
N2	34251	0.05	34251	0.07
CO2	27.5	0.05	27.6	0.002
Argon	601	0.02	601	0.003
Total	42362	2819	39738	5443
HYSYS				
H2O	2994	1967	408	4553
O2	2678	0.01	2678	0.03
Methanol	82.2	21.7	98.1	5.83
diM-Ether	173	4.13	168	9.04
Formaldehyde	1614	199	267	1546
CO	525	0.001	525	0.005
N2	36355	0.07	36355	0.29
CO2	29.2	0.003	29.2	0.01
Argon	638	0.002	638	0.009
Total	45088	2192	41166	6114
<i>Deviation</i>	<i>-2726</i>	<i>627</i>	<i>-1428</i>	<i>-671</i>

Table F5. Mass balance of the upper tank.

Upper Tank [31] Mass Balance				
Components [kg/h]	Inlet streams		Outlet streams	
	[125]	[51]	[83] Process g.	[55]
CHEMCAD				
H2O	2030	1553	826	2757
O2	0.00	2537	2537	0.01
Methanol	0.00	51.2	38.8	12.4
diM-Ether	0.00	150	146	4.46
Formaldehyde	0.00	52.8	7.50	45.3
CO	0.00	514	514	0.001
N2	0.00	34251	34251	0.05
CO2	0.00	27.6	27.5	0.05
Argon	0.00	601	601	0.002
Total	2030	39738	38949	2819
HYSYS				
H2O	1850	408	291	1967
O2	0.00	2678	2678	0.009
Methanol	0.00	98.1	76.4	21.7
diM-Ether	0.00	168	163	4.13
Formaldehyde	0.00	267	68.2	199
CO	0.00	525	525	0.001
N2	0.00	36355	36354	0.06
CO2	0.00	29.2	29.2	0.003
Argon	0.00	638	638	0.002
Total	1850	41166	40823	2192
<i>Deviation</i>	<i>180</i>	<i>-1428</i>	<i>-1874</i>	<i>627</i>

Appendix G. Energy Balances

This appendix contains the energy balances of five unit operations in the absorber as well as energy balances for compressors, pumps, heaters and coolers. The tables are only commented when the results needs further explanations.

Energy Balances of Unit Operations in the Absorber

Table G1 to G5 contains the energy balances of five unit operations in the absorber. All the energy balances in the HYSYS model gives zero accumulation, but there are some small errors in the balances of the three tanks in the CHEMCAD model. This will influence the total energy balance of the absorber to some extent. There are some variations between the energy balances in the two software, this was expected.

Table G1. Energy balance of the lower absorber.

Lower Absorber [42] Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[23] Formaldehyde	-16.5	
[64]	-47.9	
[66] Formalin		-28.5
[61]		-35.9
Total	-64.4	-64.4
HYSYS		
[23] Formaldehyde	-15.3	
[64]	-32.2	
[66] Formalin		-25.3
[61]		-22.2
Total	-47.5	-47.5
<i>Deviation</i>	<i>-16.9</i>	<i>-16.9</i>

Table 22. Energy balance of the upper absorber.

Upper Absorber [41] Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[59]		-17.6
[60]	-462	
[61]'	-35.9	
[62]		-481
Total	-498	-498
HYSYS		
[59]		-9.72
[60]	-377	
[61]'	-22.2	
[62]		-389
Total	-399	-399
<i>Deviation</i>	-99	-99

Table G3. Energy balance of the lower tank.

Lower Tank [33] Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[53]		-15.4
[56]'	-23.0	
[57]		-25.7
[59]'	-17.6	
Total	-40.7	-41.1
HYSYS		
[53]		-13.4
[56]'	-22.0	
[57]		-17.4
[59]'	-9.72	
Energy stream Tank 33	0.956	
Total	-30.8	-30.8
<i>Deviation</i>	-9.9	-10.3

Table G4. Energy balance of the middle tank.

Middle Tank [32] Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[55]'	-12.2	
[53]	-15.4	
[56]		-23.0
[51]		-6.55
Total	-27.6	-29.6
HYSYS		
[55]'	-8.97	
[53]	-13.4	
[56]		-22.0
[51]		-2.87
Energy stream Tank 32	-2.48	
Total	-24.9	-24.9
<i>Deviation</i>	-2.70	-4.70

Table G5. Energy balance of the upper tank.

Upper Tank [31] Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[125]	-8.94	
[51]	-6.55	
[55]		-12.2
[83] Process gas		-3.90
Total	-15.5	-16.1
HYSYS		
[125]	-8.13	
[51]	-2.87	
[55]		-8.97
[83] Process gas		-2.26
Energy stream Tank 31	-0.236	
Total	- 11.2	- 11.2
<i>Deviation</i>	-4.3	-4.2

Compressor

Table G6 and G7 contains the energy balances of compressor C-7 and C-4 respectively. All the energy balances in the HYSYS and CHEMCAD model gives zero accumulation. There are some variations between the energy balances in these two softwares.

Table G6. Energy balance of compressor C-7.

Compressor C-7 [201] Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
AIR INLET [154]	-0.282	
[132]		-0.200
Energy stream eC	0.0818	
Total	-0.200	-0.200
HYSYS		
AIR INLET [154]	-0.280	
[132]		-0.178
Energy stream eC	0.102	
Total	-0.178	-0.178
<i>Deviation</i>	<i>-0.022</i>	<i>-0.022</i>

Table G723. Energy balance of compressor C-4.

Compressor C-4 [206] Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[138]	-2.90	
[129]		-2.37
Energy stream eC'	0.544	
Total	-2.36	-2.37
HYSYS		
[138]	-1.78	
[129]		-1.23
Energy stream eC'	0.550	
Total	-1.23	-1.23
<i>Deviation</i>	<i>-1.13</i>	<i>-1.14</i>

Pump

Table G8 and G9 contains the energy balances of pump P-4D and P-4ABC respectively. All the energy balances in the HYSYS and CHEMCAD model sums to zero. In CHEMCAD the pump P-4D is in-between a buffer tank system, this was simplified in HYSYS. Thus, the flows connected to the pump has large deviations between the two simulation softwares.

Table G8. Energy balance of pump P-4D.

Pump P-4D [46] Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[68]	-236	
[69]		-236
eP'	3.48e-04	
Total	-236	-236
HYSYS		
[66] Formalin	-25.3	
[110]		-25.3
eP'	4.20e-05	
Total	-25.3	-25.3
<i>Deviation</i>	<i>-211</i>	<i>-211</i>

Table G9. Energy balance of pump P-4ABC.

Pump P-4ABC [8] Energy Balance		
Streams	In [MW]	Out [MW]
CHEMCAD		
[10] Formalin'	-433	
[11]		-433
eP	6.74e-04	
Total	-433	-433
HYSYS		
[10] Formalin'	-357	
[11]		-357
eP	7.50e-04	
Total	-357	-357
<i>Deviation</i>	<i>-76</i>	<i>-76</i>

Heaters and Coolers

The prevaporizer (E-3), the vaporizer (E-1), the steam generator (E-7) and one heat exchanger (E-30), were all modelled as coolers and heaters in the HYSYS model. In CHEMCAD, this equipment were modelled as heat exchangers, and no external heat flows were added. For this reason the heaters and coolers in HYSYS is not compared to the unit operations in CHEMCAD, but the overall energy streams in HYSYS should sum up to zero. As Table G10 shows this is not the case. It is likely that the deviation of -1.84 MW has its origin in the manual adjustments of the absorber.

Table G10. *The energy flows in coolers and heaters in the HYSYS model.*

Coolers and Heaters, Energy Balance		
Streams	In [MW]	Out [MW]
HYSYS		
Cooler E-3c,7c,30h		2.42
Cooler E-30c		0.16
Cooler E-1c		2.33
Heater E-3h,1h	3.07	
Total	3.07	4.91