

# Simulation of propionaldehyde production from glycerol

by

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# Abstract

The environmental awareness of the modern society of today, in combination with rising prices on fossil fuel has made it desirable to develop new and innovative processes that are sustainable alternatives to their fossil fuel based counterparts. An increasing worldwide production of biodiesel brings large amounts of the by-product glycerol to the market. This thesis will present and evaluate a new process developed by Biofuel-solutions for production of propionaldehyde from glycerol via acrolein.

The conversion of glycerol into acrolein has been known for long, but for economic reasons the reaction has not been applied industrially. In 2005, Ulgen and Hoelderich discovered the high activity of  $W\text{O}_3/\text{ZrO}_2$  catalysts for the dehydration of glycerol, a method that gave promising acrolein yields of 73–80 %. Propionaldehyde is then obtained from acrolein by hydrogenation.

Aspen Plus<sup>®</sup> that was used to simulate the process is one of the many process optimization solutions provided by Aspen Tech. The simulation models the mass and thermal balances under steady state conditions. This simulation is used to perform a parametric study where a number of modifications are made to some of the process parameters. The change in utility use is studied for each modification and the results are compared against the other modifications and the unmodified process, the base case. The process parameters that are to be modified are listed below.

- Glycerol concentration in the feed
- Hydrogen-to-glycerol ratio
- Acrolein yield

Further evaluation of the process plant and the results from the simulations is conducted with an economic evaluation. This study includes calculations of the process plant investment cost using the Hand method. It also includes gross production price and annuity calculations.

The parameter that has the largest impact on the process profitability is the glycerol concentration in the feed. Values from parametric study showed that the utility-use significantly decreased when the concentration of glycerol in the feed was increased. Best results were obtained with a glycerol concentration of 40 %. This configuration gave the lowest propionaldehyde gross production price of 8 000 SEK/tonne and the largest annual annuity surplus of 11.0 MSEK in comparison to the base case. The least promising results were obtained when the acrolein yield was lowered with 3 % in relation to the base case. This configuration gave the highest propionaldehyde gross production price of 10 100 SEK/tonne and an annual annuity deficit of 4.0 MSEK in comparison to the base case. None of the remaining process modifications leads to any prominent changes in neither utility use or economical deficit or surplus.



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# 1 Introduction

In the modern society of today where words such as environmental awareness and sustainability are used more frequently, it has never been more desirable to find new innovative and better uses for what was previously considered to be undesired by-products that are either sold with minor profit or used as fuel in the main process. Glycerol, most of which is obtained when producing biodiesel, has for a long time been viewed as such a by-product. However, in the quest to find sustainable process alternatives that are not dependent on the availability of fossil fuels, more eyes have turned to the different possibilities that glycerol may provide. The rising prices of fossil fuel, combined with increase in biodiesel production, have made glycerol more economically interesting. Glycerol also benefits from the fact that it is a versatile trivalent hydrocarbon.

This thesis will present and evaluate a new process developed by Biofuel-solutions for production of propionaldehyde from glycerol. The general concept is to react glycerol together with hydrogen over a series of catalysts to first form acrolein and then finally propionaldehyde, see figure 1.



Figure 1.1 From glycerol to propionaldehyde.

A simulation of the process plant with a production capacity of 10 000 tonnes per year will be made using Aspen Plus<sup>®</sup>. This simulation will be used to perform a parametric study where a number of modifications will be made to some of the process parameters. These parameters are the glycerol concentration in the feed, the hydrogen-to-glycerol ratio and the acrolein yield. The change in utility use will be studied for each modification and the results will be compared.

The process will be further evaluated with an economic study which includes calculations of the investment cost using the Hand method and calculations of the operating costs based on the results from the parametric study.

## 2 Background

In this section, the background of the intended study is reported.

### 2.1 Raw material, intermediate and product

The following chapter act as an introduction to the main chemical components that are present in the process when producing propionaldehyde from glycerol. The reason for reporting this is to get familiarized with the chemicals, but also to get a better understanding of the differences between existing processes and the one that has been developed by Biofuel-solution.

#### 2.1.1 Glycerol

Glycerol (1,2,3-propanetriol) is a colourless, odourless, viscous, sweet-tasting liquid and it is one of the world's most valuable chemicals thanks to its versatility<sup>1, 2</sup>. It was first discovered in 1779 by the Swedish chemist Carl W Scheele, who heated at mixture of litharge and olive oil. Glycerol was later named by Chevreul who gave it the Greek word for sweet<sup>3</sup>. The first industrial use of glycerol was in 1866 when it was used by Nobel to produce dynamite.

There is a wide range of applications for glycerol, either as an additive or as a raw material<sup>2</sup>. It is used as an additive in food, tobacco and drugs but also in the synthesis of trinitroglycerine, alkyd resins and polyurethanes. In 2008 it was estimated that the amount of glycerol used in technical applications reached 160 000 tonne/year and the use was expected to grow at an annual rate of 2.8 %.

#### ***Production***

In the late 1930s I.G. Farben and Shell developed an industrial synthesis of glycerol using propene as starting material<sup>3</sup>. Today glycerol is obtained as a by-product in the conversion of fats and oils to fatty acids or fatty acid methyl esters. The production of the later is the largest source of glycerol as the fatty acid methyl esters are used for making biodiesel.

Glycerol is obtained as a by-product in the production of biodiesel<sup>1</sup>. Figure 2.1 shows a schematic diagram of biodiesel production from feedstock's containing low levels of free fatty acids, FFA. Vegetable oils react together with methanol in the presence of an alkali catalyst and form a mixture of methyl esters and glycerol. The glycerol is separated from the methyl esters and further purged from FFA and methanol before leaving the process as crude glycerol, which is approximately 85 % pure. The methyl esters go through neutralization and methanol removal before being washed with water and then dried to form finished biodiesel.

Crude glycerol is often concentrated and purified to 95.5–99 % purity before being sold commercially<sup>2</sup>. This refining is generally accomplished by distillation and active carbon treatment<sup>1</sup>.



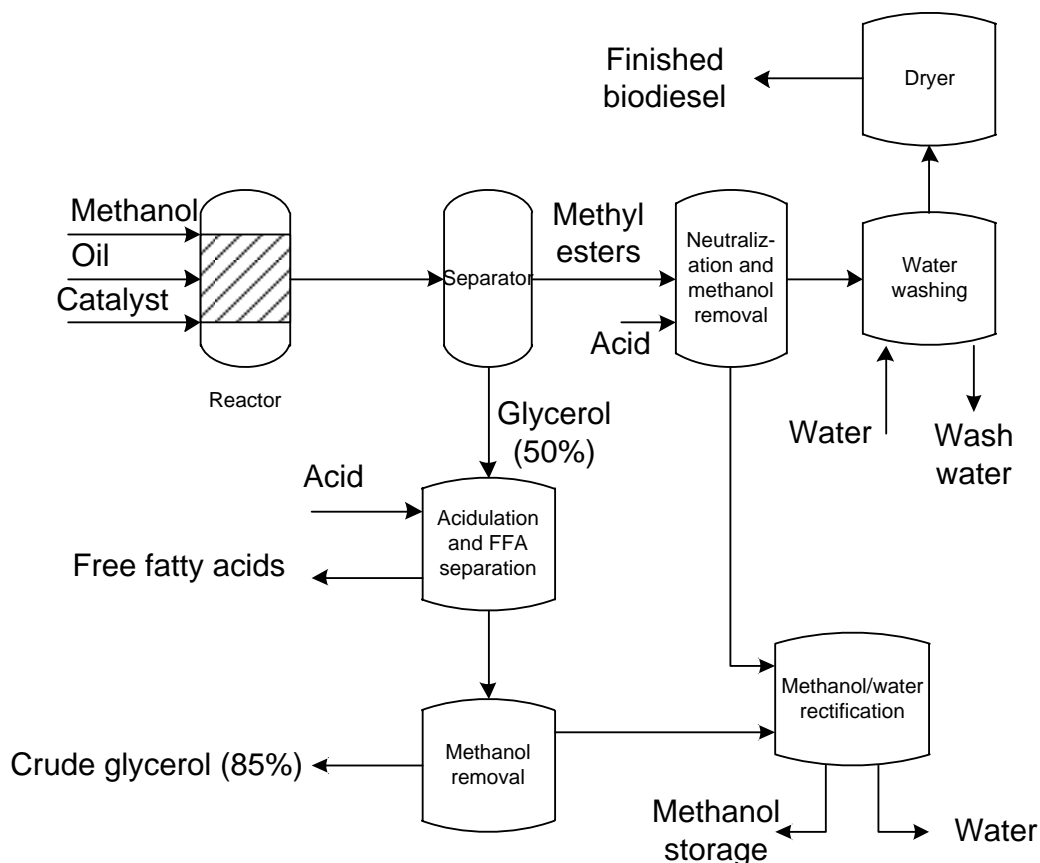


Figure 2.1. Biodiesel production

### New uses of glycerol

The increasing worldwide production of biodiesel based on triglycerides result in an increased production of glycerol, which is obtained as a by-product from the biodiesel process<sup>4</sup>. However the demand for glycerol is not increasing at the same rate. This result in lower prices on glycerol, which thereby is becoming economically and environmentally interesting as a starting material in synthesis of various compounds and new uses of glycerol are therefore being researched. Due to the rapid decline in price, glycerol is increasingly replacing other polyols, which are used in confectionery, food, oral care and pharmaceutical and industrial applications<sup>2</sup>.

Another area that has been actively researched in recent years is the esterification of glycerol. When the esterification is carried out using carboxylic acids the received products are monoacylglycerols, MAGs, and diacylglycerol, DAG. Both MAGs and DAGs are commonly used as food additives in dairy and bakery products.

Selective oxidation of glycerol is also an interesting field considering the commercial relevance of oxygenated glycerol derivatives. A newly developed gold catalyst is used in a highly selective process for production of the human metabolite glyceric acid.

A major achievement of the new glycerol chemistry is the aqueous phase reforming process, APR. In this process glycerol is converted to hydrogen and carbon monoxide, a mixture that is commonly known as synthesis gas. The reaction takes place under relatively mild conditions at temperatures between 225–300 °C using a Pt-Re catalyst in a single reactor.

Both acrolein and 3-hydroxypropionaldehyde can be produced by direct dehydration of glycerol. Also, oxydehydration of glycerol gives acrylic acid which is a commercially important chemical. A more detailed description of acrolein production from glycerol will be presented later.

### 2.1.2 Acrolein

Acrolein is the simplest unsaturated aldehyde and it is an explosive and toxic chemical whose handling requires the highest safety standards<sup>2</sup>. It was first reported in 1843<sup>5</sup> and it is primarily used as an intermediate in production of other substances<sup>6</sup>. The main part, over 90 %, of the refined acrolein that is produced today is used for methionine production<sup>5</sup>. Another major field is the production of acrylic acid which is produced by captive oxidation of crude acrolein.

The first commercial production of acrolein was established in 1942 by Degussa<sup>2, 5, 6</sup>. The method used was a heterogeneously catalysed (sodium silicate on silica support) gas-phase condensation of acetaldehyde and formaldehyde. This method prevailed until 1959 when Shell commercialized another method to produce acrolein, a vapour-phase oxidation of propylene using a cuprous oxide and cupric selenite catalyst<sup>5</sup>. In 1975, a bismuth molybdate catalyst is discovered by Standard Oil of Ohio. This new catalyst is capable of producing high yields of acrolein at high propylene conversions and at low pressures.

#### **Production**

Today, all known commercial acrolein manufacturing processes are based on propylene oxidation and use complex mixed-metal oxide catalysts based on bismuth molybdate<sup>5</sup>. Propylene conversions of 93 % to 98 % with acrolein selectivity of 85 % to 90 % are typical. Table 2.1 lists the key acrolein producers. About 350 000 tonne acrolein is produced every year worldwide.

*Table 2.1 Key acrolein producers*

<b>Company</b>	<b>Country</b>
Adisseo	France, China
Arkema	France, USA
Evonik	Germany, USA
Dow Chemical Company	USA
Daicel	Japan
Volzhskiy Orgsynthese	Russia
Baker Performance Chemicals	USA

A typical process flow diagram for acrolein production from propylene is shown in figure 2.2. The reaction is generally carried out in a fixed-bed multi-tube reactor at near atmospheric pressure<sup>5</sup>. Air is normally used as the oxygen source and steam is added to inhibit formation of flammable gas mixtures and to suppress coking. The concentration of the propylene feed is typically 7–10 mole% along with temperatures of 85–250 °C. The reaction is exothermic and generates about 418 kJ/mol. Primary by-products are acrylic acid, acetaldehyde, acetic acid, carbon monoxide and carbon dioxide. Other aldehydes and acids are formed in small amounts.

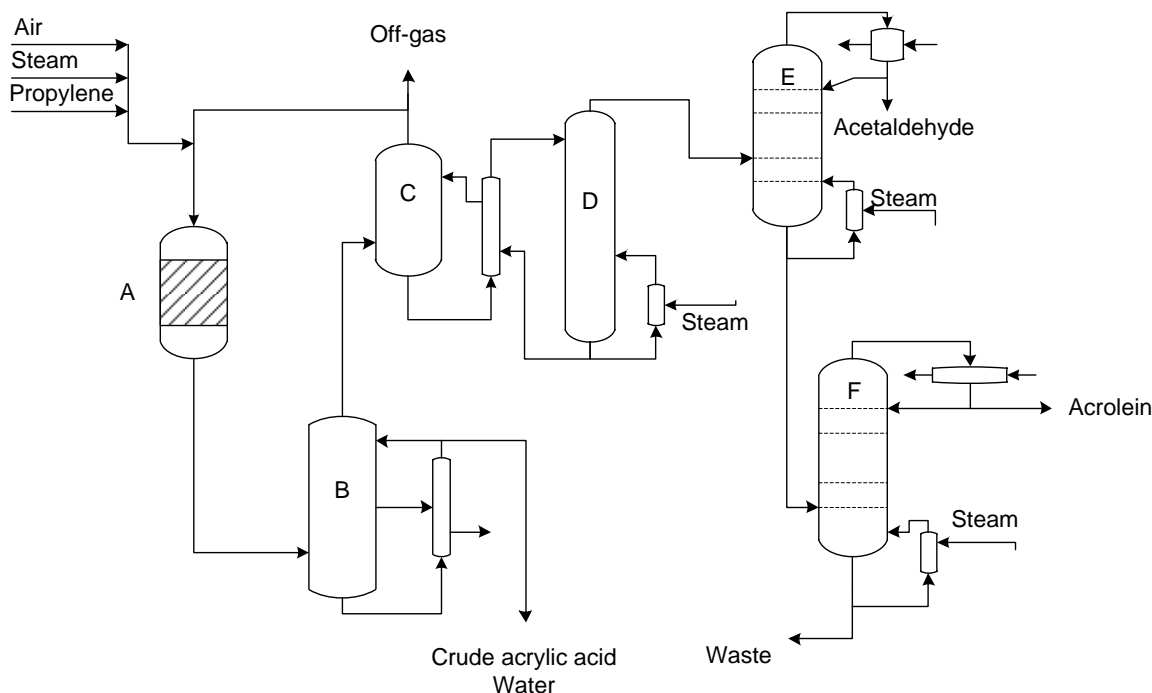


Figure 2.2. Acrolein production from propylene

### Acrolein from glycerol

The conversion of glycerol into acrolein has been known for long, but for economic reasons the reaction has not been applied industrially<sup>7</sup>. However, the price of propylene has increased greatly over the last decade, making the production of acrolein from the less expensive glycerol commercially attractive<sup>2</sup>. Shifting the raw material from propylene, which comes from crude oil, to glycerol would both encourage the production of biodiesel and avoid using fossil fuel in the production of acrolein<sup>4</sup>.

A number of different methods have been used for producing acrolein from glycerol. It was Sabatier et al. that in 1918 first reported the decomposition of glycerol to different products, including acrolein, in the presence of alumina catalysts<sup>8</sup>. Later in the year of 1930, Schering-Kahlbaum patented a process in which glycerol was dehydrated using metal phosphates impregnated on pumice stone<sup>4</sup> and the acrolein yield was claimed to be 80 %. 18 years later a heterogeneously catalysed continuous flow fixed bed process was patented by Hoyt et al. In 1993 Neher et al. produced acrolein as a first step in the production of 1,2- and 1,3-propandiol by dehydration of glycerol using phosphoric acid on an  $\alpha$ -alumina support. The yield was reported to be 70.5 %.

It has been discovered that acrolein is also formed by distillation of glycerol in the presence of a metal or salts ( $\text{MgSO}_4$ , alkali phosphates and silica) at temperatures below  $350\text{ }^\circ\text{C}$ <sup>7</sup>. A yield of 22–48 % acrolein is obtained using potassium bisulphate as dehydrating agent.

Acid catalysts such as phosphoric acid on alumina (acids with  $H_0$  between -8.2 and -3) also give satisfactory acrolein formation in both gas and liquid phase<sup>7</sup>. Gaseous glycerol (20 wt. % water) is fully converted with an acrolein yield of 70.5 % at  $300\text{ }^\circ\text{C}$ .

Non-catalysed reactions have also been performed<sup>7</sup>. Acrolein, along with acetaldehyde and carbon monoxide is obtained in pyrolysis of glycerol in steam. A temperature of 650 °C and atmospheric pressure gave a yield as high as 52 %.

### **WO<sub>3</sub>/ZrO<sub>2</sub> catalysts**

In 2005, Ulgen and Hoelderich discovered the high activity of WO<sub>3</sub>/ZrO<sub>2</sub> catalysts for the dehydration of glycerol in gas phase using a continuous flow fixed bed reactor under atmospheric pressure<sup>4</sup>. Promising results were achieved with acrolein yields of 73–80 % and total conversion of glycerol. The experiments were performed using WO<sub>3</sub>/ZrO<sub>2</sub> catalysts with five different WO<sub>3</sub> contents between 2.11 and 15.43 wt.% WO<sub>3</sub>.

To determinate the optimal reaction temperature, an initial series of experiments were performed with unmodified WO<sub>3</sub>/ZrO<sub>2</sub> pellets with 19 wt. % WO<sub>3</sub>. It was found that glycerol is extensively converted at temperatures higher than 240 °C; however the selectivity of acrolein reached a maximum at 280 °C. At temperatures below 280 °C the formation of glycerol oligomers is thermodynamically favoured over the formation of acrolein. At temperatures above 280 °C the formation of carbon monoxide and carbon dioxide is possible. Due to obtained results 280 °C was selected as standard temperature when testing the WO<sub>3</sub>/ZrO<sub>2</sub> catalysts.

ZrO<sub>2</sub> is an amphoteric material; it can have both acidic and basic sites. By adding various amounts of WO<sub>3</sub> the acidic/basic sites are modified. The corresponding effect on the catalytic performance for the dehydration of glycerol was studied. An increase in the amount of WO<sub>3</sub> led to an increasing acrolein selectivity starting from 11.3 % for 2.11 wt.% WO<sub>3</sub> to 55.3 % for 15.43 wt.% WO<sub>3</sub>. This shows that a high acrolein selectivity is favoured by the existence of weak acidic sites as well as the absence of basic sites. The opposite conditions enable a higher selectivity of undesirable hydroxyacetone.

Lastly the effect of calcination was studied. These catalysts were screened using the same conditions as the uncalcined predecessors. It appears that the increase in pore size of the catalysts has a positive effect on the transport phenomena thus increasing the conversion of glycerol considerably. The selectivity of acrolein also increased.

The results from the experiments with the various catalysts are summarized in table 2.2. It contains the conversion of glycerol as well as the selectivity of acrolein and various by-products.

*Table 2.2. Results from experiments with different WO<sub>3</sub>/ZrO<sub>2</sub> catalysts*

WO <sub>3</sub> amount (wt.%)	Calcination	Conversion (%)	Selectivity (%)			
			Acrolein	Propion aldehyde	Hydroxy acetone	Others
5.31	Before	37.7	27.8	1.0	41.5	29.7
5.31	After	47.5	64.8	1.2	15.9	18.1
9.17	Before	38.2	35.2	1.1	29.7	34.0
9.17	After	95.6	62.3	1.4	9.5	26.8
15.43	Before	57.7	55.3	1.5	25.1	18.1
15.43	After	88.7	72.1	0.8	10.3	16.8

As a conclusion it can be said that Ulgen and Hoelderich found that the production in a continuous manner of acrolein by dehydration of glycerol was shown to be possible.  $\text{WO}_3/\text{ZrO}_2$  catalysts are deemed suitable for use in this process. The optimal reaction temperature is 280 °C as this minimizes the occurrence of side reactions producing unwanted by-products. Acrolein selectivity is favoured by the existence of weak acidic sites while basic sites increase the production of hydroxyacetone. Thus, the catalytic properties are improved by an increasing amount of  $\text{WO}_3$  in the catalyst. Lastly it was proven that the catalytic performance was enhanced by calcination.

### 2.1.3 Propionaldehyde

Propionaldehyde, PA, also known as propanal, is a colourless, flammable liquid with a sharp and suffocating odour<sup>9</sup>. It occurs naturally in vegetables such as onions and in some dairy products. Propionaldehyde is highly reactive and occurs as a chemical intermediate when preparing C-3 and C-6 compounds. There is no direct use of propionaldehyde but it is primarily converted into 1-propanol, propionic acid and thrimethylolethane.

#### **Production**

The most used process for production of propionaldehyde is the low-pressure rhodium-catalysed hydroformulation of ethylene with carbon monoxide and hydrogen. Another method is the one mostly used in Europe where cobalt is used as a catalyst instead of rhodium. This process however has to be carried out at a higher pressure than the one using the rhodium catalyst.

The low-pressure hydroformulation process uses a soluble rhodium catalyst complex with excess triphenylphosphine. The reaction occurs in the liquid phase at a temperature between 90–130 °C and a total pressure of below 2.8 MPa. Since ethylene can lead to only one isomer and impurities can be minimized, the process has a very high selectivity, over 90 %. The production of by-products is inhibited by exclusion of oxygen, organic acids and Lewis-acid catalysts such as iron.

Propionaldehyde can also be produced from acrolein and this is the method that will be used in this study<sup>10</sup>. By hydrogenating acrolein, propionaldehyde is obtained together with n-propylalcohol and allyl alcohol. The selectivity can be steered to any of the three products by a carefully chosen catalyst. The main products with corresponding catalysts are listed in table 2.3.

*Table 2.3. Products from hydrogenation of acrolein with corresponding catalysts*

<b>Product</b>	<b>Catalyst</b>
1-propanol	Ni
Propionaldehyde	Pd
Allyl alcohol	Pt, Os or Cu/Cr or Cd/Zn

## 2.2 Aspen Plus<sup>®</sup> introduction

Aspen Plus<sup>®</sup> is one of the many process optimization solutions provided by Aspen Tech<sup>11</sup>. It is a versatile computing tool that allows users to simulate actual plant behaviour, using realistic operating conditions, accurate equipment models thermodynamic data together with a vast range of engineering relationships, such as mass and energy balances, phase and chemical equilibrium and reaction kinetics. Aspen Plus<sup>®</sup> enables companies to reduce capital and operating costs and to maximize plant performance and profitability.

### 3 Process description

Figure 3.1 shows a process flow diagram for the production of propionaldehyde using glycerol as a starting material. The conversion is carried out in two steps. First the glycerol undergoes a dehydration step and is converted into acrolein. Then the acrolein is hydrogenated and forms propionaldehyde. Both reactions are carried out in gas phase.

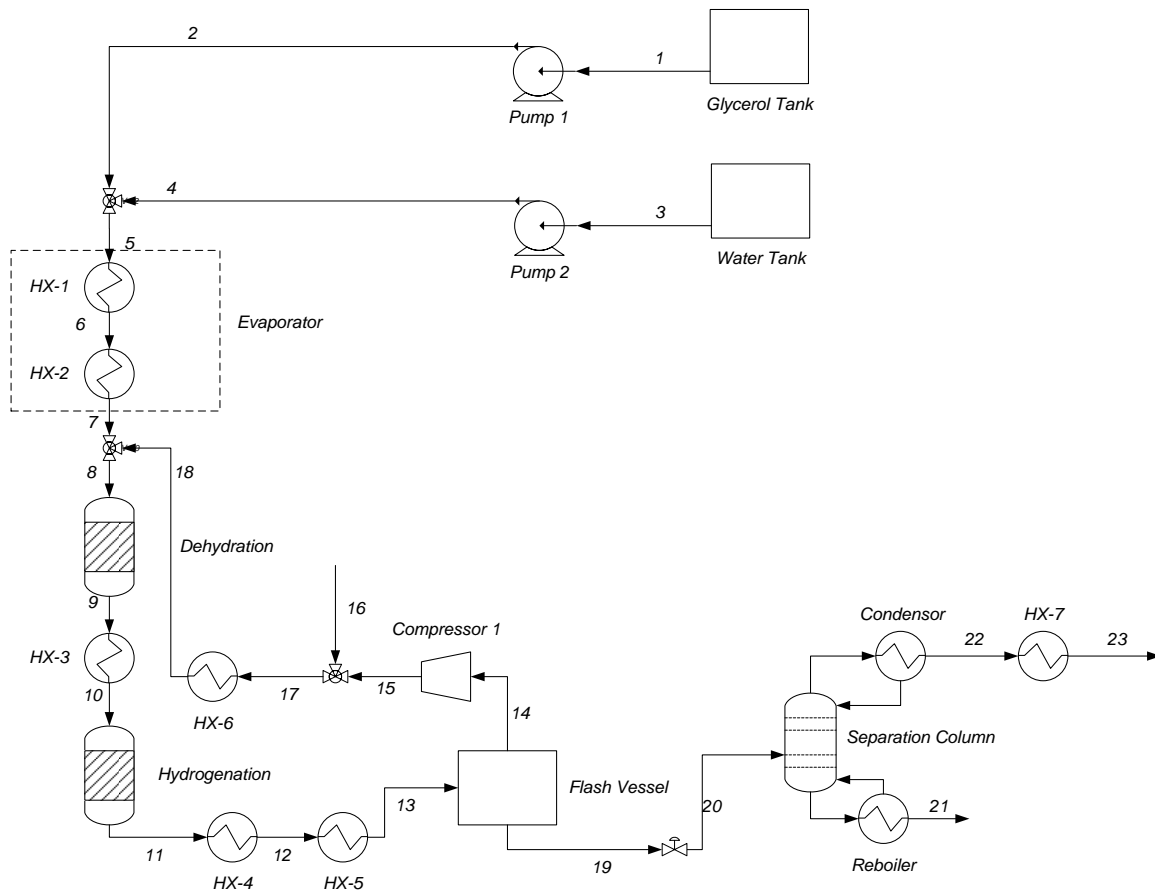


Figure 3.1. Propionaldehyde production from glycerol

Crude glycerol (80 wt. %) is diluted with water to 20 wt. % before entering an evaporator. The solution also contains approximately 10 wt. % sodium sulphate, which is removed in the evaporator. A boiling point elevation will occur due to the salt. The evaporator is powered by high-pressure steam.

Hydrogen is added to the reactant mixture at a molar ratio of 1 mole of glycerol to 4 moles of hydrogen before entering the first reactor. This is an adiabatic fixed bed reactor containing a dehydration catalyst for converting of glycerol into acrolein at 250 °C. The conversion of glycerol is 100 % and apart from acrolein (85 mole%), small amounts of propionaldehyde (10 mole%) and hydroxyacetone (5 mole%) are also formed.

The reaction mixture is cooled down, using cooling water, to 180 °C before entering the second reactor. This is a fixed bed reactor containing a hydrogenation catalyst for conversion of acrolein into propionaldehyde. The conversion of acrolein is 100 % and the selectivity for

conversion into propionaldehyde is 100 %. This brings the total yield of propionaldehyde up to 95 mole% and 5 mole% hydroxyacetone.

The product mixture is cooled down to 30 °C in two steps before entering a flash vessel for removing the excess hydrogen from the liquid products. Small amounts of water, propionaldehyde and hydroxyacetone will be found in the hydrogen. The excess hydrogen is compressed and mixed with make-up hydrogen before entering the reactant stream before the first reactor. By cooling the product mixture from the second reactor in two steps it is possible to obtain low-pressure steam that can be used to power other units in the process.

The liquid phase that leaves the flash vessel contains water, propionaldehyde, hydroxyacetone and small amounts of hydrogen. It passes through a pressure valve before entering a distillation column which is used to separate the propionaldehyde from the other components. Propionaldehyde leaves the column in a gaseous phase while the waste water and organic waste leaves column in liquid phase. The column reboiler can be powered by the previously produced low-pressure steam.

## 4 Aspen Plus<sup>®</sup> simulation

The advantages of simulating a process with the help of computing power as opposed to performing the calculations by hand are many. A good model can provide a prediction of how the system behaves on a larger scale and allows the user to make small adjustments with little effort. It is easy to obtain approximate values for parameters such as stream sizes, pressure, temperatures, heat duty etc. There is also the possibility to estimate energy consumption and operating costs. Also Aspen Plus<sup>®</sup> uses extensive chemical data bases which contain information that normally could be very time consuming to collect from other sources.

This chapter contains a simulation of the mass and thermal balances of the propionaldehyde process under steady state conditions. The underlying process scheme used for the simulation, along with approximate parametric values, was all provided by Biofuel-solution.

### 4.1 Assumptions and simplifications

A number of simplifications and assumptions regarding the process were made to facilitate the simulation.

It is assumed that the yields that were obtained in the laboratory experiments also apply in full scale production. Whether this assumption is correct or not, cannot be determined without tests being performed on a larger scale.

Further it is assumed that the inflow is free from salt and thus only contains glycerol and water. By doing this, the boiling point elevation that normally would occur due to the salt when evaporating the input flow can be disregarded. Further the evaporator unit has been simulated as a heater.

There is currently no bleed stream in the process which results in a smaller amount of added make-up hydrogen. Indirectly it also implies that there is no accumulation of impurities in the process which is highly improbable.

The simulation uses the Wilson model, since the equilibrium curve obtained when doing test simulations for the distillation column was the one that closest resembled equilibrium curves published in literature<sup>12</sup>. Also, no phase separation occurs when using the Wilson model which simplifies the simulation further.

Another simplification that was made is that the simulation does not take into account the heat loss that is present throughout the process.

When simulating the heat exchangers and the evaporator the pre-set heat transfer coefficients,  $U$ , were replaced by estimated values based on experience and rules of thumb.



## 4.2 Simulation

Figure 4.1 shows the process scheme that was used in the Aspen Plus<sup>®</sup> simulation.

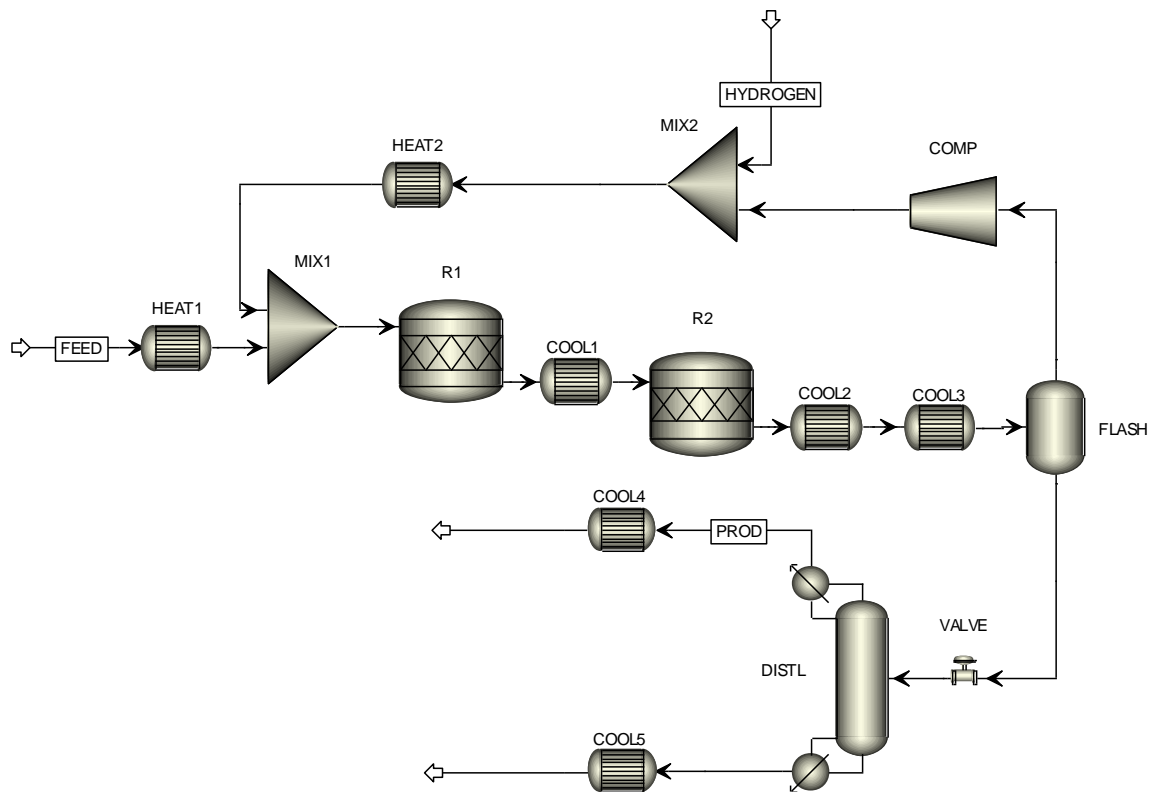


Figure 4.1. Aspen Plus<sup>®</sup> process scheme for propionaldehyde production from glycerol

After test running the model, a few changes were made to the original process. Temperatures had to be adjusted to ensure that the reactant mixture remained in gaseous phase and not condensed inside the reactors. Instead of setting a fix temperature it was specified that the outgoing streams should have a vapour fraction of 1. This ensures that the reactant mixture remains in gaseous phase even if changes of the ratio in the feed are made. Another change that was made was that a cooler was added to cool the waste stream from the distillation column. Also the temperature of the stream entering the flash unit was increased so that cooling water could be used to lower the stream temperature instead of another refrigerant.

The model uses three design specifications. The first calculates the feed amount needed to achieve a yearly production of 10 000 tonne PA/year. Production standstill due to maintenance has been taken into consideration and it is therefore specified that the plant is running 8000 h/year. The second design specification determines how much make-up hydrogen must be added to fulfil specific hydrogen-to-glycerol molar ratios in the second reactor. The third design specification was previously mentioned and ensures that the vapour fraction of the reactant mixture is 1.

This model and its configurations is what will later be used as the base case in the parametric study. Of special notice are the configurations of the glycerol concentration in the feed, the hydrogen-to-glycerol ratio, and the acrolein yield in the first reactor, values are listed in table 4.1. These parameters will later be modified when performing the parametric study.

Table 4.1. Values of base case parameters

Parameter	Value
Glycerol concentration in feed	20 %
Hydrogen-to-glycerol ratio	4:1
Acrolein yield in first reactor	85 %

### 4.3 Utilities

The simulation uses a number of utilities to heat and cool the different units of the process. Both heaters, HEAT1 and HEAT2, uses high-pressure steam while all coolers, including the condenser in the distillation column, use cooling water with an inlet temperature of 20 °C. As mentioned earlier in the process description, COOL2 can be used to produce low-pressure steam and this is the case in the simulation. Part of the produced low-pressure steam powers the reboiler in the distillation column and the excess steam can be sold. The cooling water leaving COOL1 and COOL3 holds a temperature of 90 °C. This water can be used for district heating, provided that the plant is located near a district heating network. Since the first reactor is adiabatic it has no need for any utility. The second reactor on the other hand is in need of cooling, but no utility has been specified for this task. Lastly the compressor is powered by electricity.

## 5 Process evaluation

To evaluate the process it was decided to conduct a parametric study and also an economic evaluation of the results.

### 5.1 Parametric study

A parametric study was performed to examine how the usage of the various process utilities changed with different operating conditions. The information obtained from this study can be used to optimize the plant's energy consumption and operation costs. By varying specified operation conditions one at the time and comparing the results with a predetermined base case, it is possible to see what impact the different scenarios have on the system. The modified and studied parameters are listed below.

#### Modified parameters

- Water to glycerol ratio in feed
- Hydrogen to glycerol ratio entering the first reactor
- Acrolein yield in first reactor

#### Studied parameters

- High-pressure steam
- Low-pressure steam
- Electricity
- Cooling Water
- District Heating
- Organic waste
- Glycerol

### 5.2 Economic evaluation

To better comprehend the impact of the different scenarios in the parametric study, it is advantageous to study the results from an economic point of view. This will be done in two different ways. In the first study, a gross production price of propionaldehyde will be calculated. This price is a measurement of how much one tonne of propionaldehyde must cost to cover the utility expenses that are generated when producing one tonne of propionaldehyde in the different scenarios. These utility costs are calculated using the results from the parametric study combined with today's utility prices. The prices that were used were current in February 2012 and are listed in table 5.1. Since cooling water is relatively inexpensive and will not affect the operating costs to any great extent it has been disregarded in the calculations.

Table 5.1. Utility costs from February 2012

Utility	Price
Electricity	1 SEK/kWh
High-pressure steam	270 SEK/tonne
Low-pressure steam	135 SEK/tonne
District heating	170 SEK/MWh
Glycerol	2250 SEK/tonne
Hydrogen	22500 SEK/tonne
Propionaldehyde	13500 SEK/tonne
Water treatment	14103 SEK/tonne

Utility costs are only a part of the total operating cost. Other costs that are included in the operating cost are the costs for storage, maintenance and repairs, spare parts, operating labour, management, laboratory work, overhead, administration, etc.

The second study uses the annuity method to compare the annuity for the different simulation scenarios. This method requires that the investment cost for erecting the plant is known. An investment cost estimation for the production plant developed by Biofuel-solutions, figure 3.1, with an annual production capacity of 10 000 tonne will be made using the Hand method.

### 5.2.1 Hand method and price updating

The investment cost has been estimated using the Hand method that was published by W.E. Hand in 1958<sup>13</sup>. Using this method, the capital cost is obtained by multiplying the purchase cost of each needed piece of equipment with its Hand factor and then summing these. This capital cost is only valid for equipment made out of carbon steel and it does not include instrumentation costs, construction costs, contingencies and other factors that affect the final investment costs. To include these costs, the capital cost is corrected with a number of published factors and percentages based on rules of thumb<sup>14</sup>.

Correction factors<sup>13</sup>

- $F_m$  – Material adjustment factor
- $F_i$  – Instrumentation factor
- $F_b$  – Building factor
- $F_p$  – Place factor

Supplement charges based on rules of thumb<sup>14</sup>

- 25 % of total cost for auxiliary buildings and equipment
- 15 % of total cost for construction and contingencies

Hand factors<sup>13</sup> that were used in the estimations are listed in table 5.2.

Table 5.2. Hand factors

Equipment type	Hand factor
Fractionating columns	4
Pressure vessels/tanks	4
Heat Exchangers	3.5
Compressors	2.5
Miscellaneous equipment	2.5

Since all unit operations in the plant will be made from stainless steel the same material- adjustment factor will be used when doing the purchase cost calculations. The material- adjustment factor is based on the cost ratio of the intended construction material and carbon steel. This ratio is then used in a diagram developed by Clerk in 1963<sup>13</sup>. Material adjustment factor  $F_m = 0.55$  will be used in the purchase cost calculations.

The instrumentation factor is a function of the amount of instrumentation in a process or plant. A plant using central control is given the instrumentation factor  $F_i = 1.55$  and it is this factor that will be used in the purchase cost calculations.

Hand factors do not account for any building costs. This is rectified with the help of a building factor. The building factor depends on if the plant processes solids, fluids or a combination of the two and also if it is a new plant that is to be constructed or if it is an expansion to an existing plant. In this case a new plant processing solids and fluids is to be built. The building factor  $F_b = 1.47$  will be used in the purchase cost calculations.

If the plant is to be located outside the U.S., a place factor is used to adjust the costs for the intended country. This factor may not be reliable since the economic conditions in other countries relative to the U.S. have changed since the factors were published in 1996<sup>13</sup>. Germany is chosen as the building location for this plant and this gives the place factor  $F_p = 1.05$  which will be used in the purchase cost calculations.

The costs in their final form:

$$\text{Capital cost} = \Sigma[\text{Equipment purchase cost} \cdot (\text{Hand factor} \cdot F_m)] \cdot F_i \cdot F_b \cdot F_p \quad (1)$$

$$\text{Investment cost} = \text{Capital cost} \cdot 1.25 \cdot 1.15 \quad (2)$$

Since the data used in the equipment cost estimation is from 2005 and thereby somewhat outdated, the cost has to be adjusted for inflation using the Chemical Engineering Plant Cost Index<sup>12</sup>, CEPI. The relation between cost and CEPI is described in equation 3.

$$\frac{\text{Cost at time 2}}{\text{Cost at time 1}} = \frac{\text{CEPI at time 2}}{\text{CEPI at time 1}} \quad (3)$$

Table 5.3 lists the Chemical Engineering Plant Cost Index's that were used in the calculations<sup>15</sup>.

*Table 5.3. CEPI used in economic calculations. \*This value is lower than the actual CEPI for 2005 but it is the value used in the price estimation data.*

Year	CEPI
2005	460*
2010	550.8

### 5.2.2 The annuity method

The annuity method<sup>14</sup> was used when doing the economic calculation, equation 4 and 5. This method calculated the annuity,  $N_I$ , as a function of profit,  $a$ , and the investment cost,  $G$ , where  $f_A$  is the so called annuity factor. The annuity factor is a function of the economic lifespan,  $N$ , and the depreciation,  $X$ .

$$N_I = a - f_A \cdot G \quad (4)$$

$$f_A = \frac{X}{1 - (1+X)^{-N}} \quad (5)$$

It is specified that the plant developed by Biofuel-solutions have an economic lifespan of ten years and a depreciation of 5 %.

### 5.2.3 Assumptions and simplifications

Some specifications regarding the equipment were made when estimating equipment size and cost. The storage capacity is presumed to be able to hold raw materials, product and waste for five days of uninterrupted production. Values for gas hourly space velocity, GHSV, used when calculating reactor sizes are estimated from experience. All heat exchangers are of U-tube type and the evaporator is falling-film. All other values needed for size estimations, such as volume flow, density, areas etc., were taken from the simulation.

The Hand method was not used when estimating the equipment cost for the falling-film evaporator, this because the used literature did not contain this specific piece of equipment. Instead the cost was estimated using the Ulrich method. This estimated cost will correspond to the value inside the square brackets in equation 5.1 and can therefore be used when calculating the capital cost using the Hand method.

It is also assumed that the plant will be a brown-field erection. This means that no self-production of high-pressure steam or hydrogen will be needed. Instead, these goods will be provided by pipelines.

Apart from utility costs, the rest of the components that make up the total operating cost have not been specified. This means that accurate calculations of the annuity for the different simulation outcomes cannot be made. To circumvent this problem an estimation of these additional operating costs can be made by assuming that the annuity for the base case is zero. By doing this, equation 4 can be modified into equation 6 and the additional operating costs can be calculated with equation 7.

$$0 = (\text{Income} - \text{Utility costs} - \text{Additional operating costs}) - f_A \cdot G \quad (6)$$

$$\text{Additional operating costs} = \text{Income} - \text{Utility costs} - f_A \cdot G \quad (7)$$

If this additional operating cost is assumed to be valid for all different simulation scenarios, the annuity can be calculated for the different simulation scenarios using equation 5. This method gives an indication if the modification made in the process results in a larger or smaller profit compared to the process being operated with the base case configurations.

## 6 Results and discussion

The results from the parametric study and the economic evaluation are presented and commented in this chapter.

### 6.1 Parametric study

Tabulated values from the parametric study can be found in appendix A. To better illustrate the outcome of the parametric study the results are presented graphically in figures 6.1-6.3 below.

#### 6.1.1 Glycerol concentration

Figure 6.1 contains the results from the scenario where the concentration of glycerol in the feed was varied. As the figure shows the electricity and glycerol consumption, together with the amount of organic waste, remains unchanged while the value of the other parameters decreases throughout the scenario.

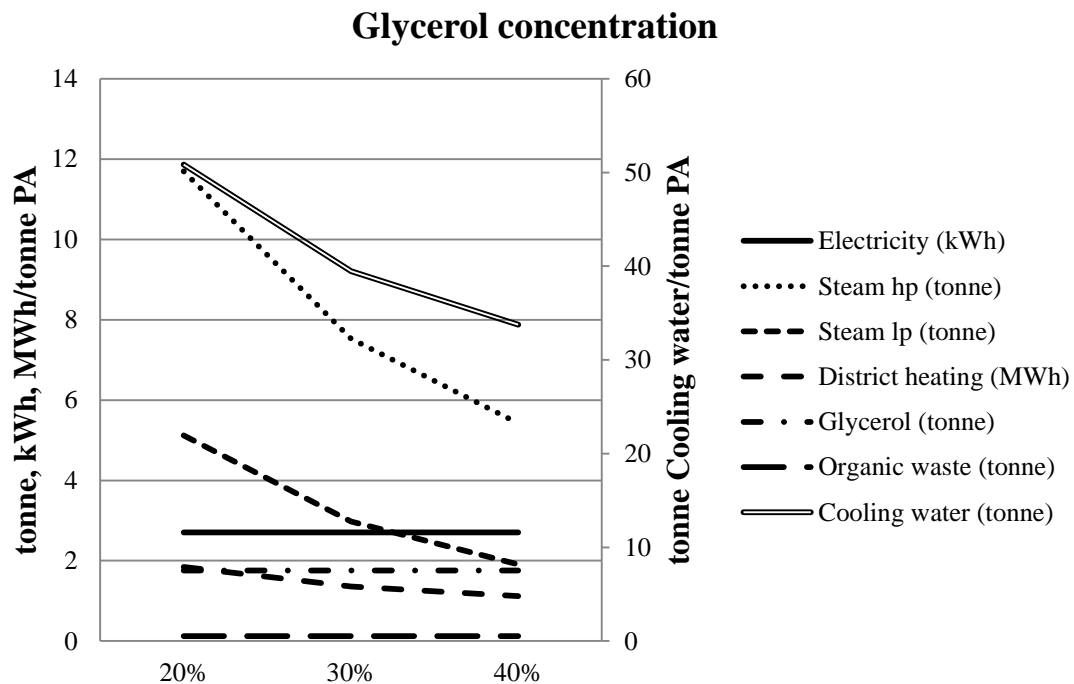


Figure 6.1. Results from scenario with varied glycerol concentration

Most prominent is the decrease of high-pressure steam, which have more than halved. The decrease in high-pressure steam usage is due to the fact that glycerol has a lower specific heat capacity than water and thus a smaller amount of high-pressure steam is needed and the same reasoning can be applied when explaining the decrease in the amount of cooling water needed. Also, the reduced production of low-pressure steam and district heating directly linked to the decrease of cooling water usage. Neither the consumption of electricity and glycerol, nor the amount of organic waste are linked to the glycerol content in the feed, and thus remain unchanged throughout the scenario.

### 6.1.2 Hydrogen-to-glycerol ratio

Figure 6.2 contains the results from the scenario where the hydrogen-to-glycerol ratio entering the first reactor was varied. As the figure shows the glycerol consumption and the amount of organic waste remains unchanged throughout the scenario. There is a steady increase in consumption of high-pressure steam, electricity and cooling water and in the production of district heating while there is a small decrease of low-pressure steam.

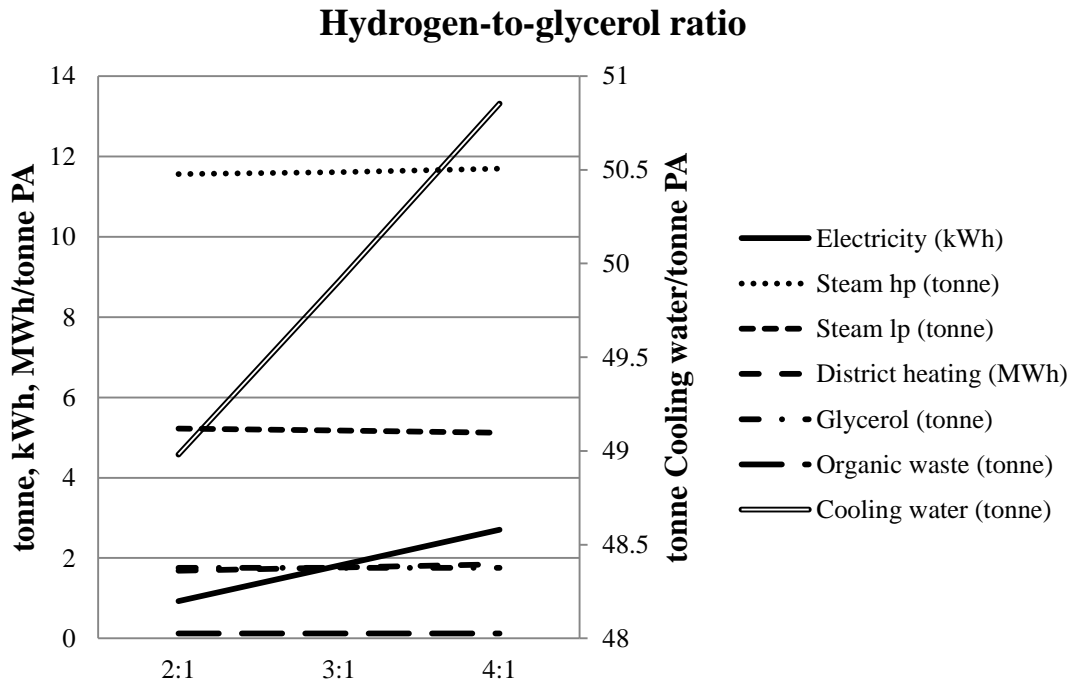


Figure 6.2. Results from scenario with varied hydrogen-to-glycerol ratio

The increase in consumed amounts of high-pressure steam, electricity and cooling water is directly linked to the increasing hydrogen flow. A higher hydrogen ratio means a larger gas volume that must be compressed and heated, hence the linear increase in electricity and high-pressure steam usage. The same reasoning is true for the increase in cooling water usage. Even though the cooling water usage is increasing with higher hydrogen to glycerol ratios, the production of low-pressure steam is decreasing. This can be a result of the increasing amount saturated steam. A larger fraction of saturated steam gives less condensate and thus less energy is needed to cool the stream. Due to the small amount of hydrogen when using the 2:1 ratio the temperature of the second reactor had to be increased by 5 °C to ensure that the reaction mixture stayed in gaseous phase in the reactor. This could be another reason for the decrease occurring when changing the ratio from 2:1 to 3:1. Since neither the glycerol consumption nor the amount of organic waste are not linked to the hydrogen to glycerol ratio it remains unchanged throughout the scenario.



### 6.1.3 Acrolein yield in first reactor

Figure 6.3 contains the results from the scenario where the acrolein yield in the first reactor was varied. As the figure shows a there is a steady decrease in all parameters with increasing acrolein yield.

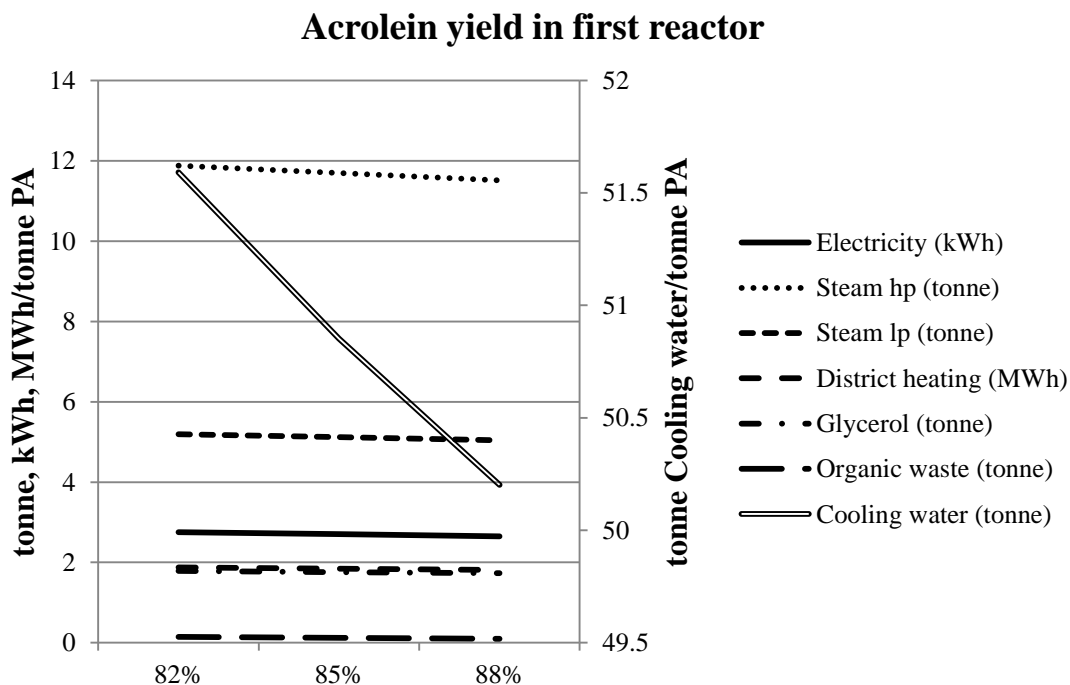


Figure 6.3. Results from scenario with varied acrolein yield in first reactor

An increase of acrolein yield in the first reactor means that a smaller amount of glycerol is needed for each tonne PA produced. This automatically entails that less feed is needed with increasing acrolein yield and thus the need for electricity, high-pressure steam and cooling water decreases throughout the scenario. Production of low-pressure steam and district heating is directly linked to the cooling water usage. The amount of organic waste decreases due to the fact that the amount of produced hydroxyacetone decreases with increasing acrolein yield.

## 6.2 Economic evaluation

Calculations regarding the propionaldehyde gross production price calculations are presented in appendix B. Calculations regarding the investment cost are presented in appendix C. Calculations regarding the operating costs and annuity comparison are presented in appendix D.

### 6.2.1 Propionaldehyde gross production price

Figure 6.4 contains the results from the gross production price calculations. The bars clearly show the individual cost contributions of the different utilities. Since the hydrogen consumption is the same in all cases, so is its contribution in the figure. The electricity contribution is so small that it is not visible in the figure. Also, it can be seen that the difference in gross production price between the different cases is mostly attributable to the amount of high-pressure steam that is used in each case.

## Gross production price

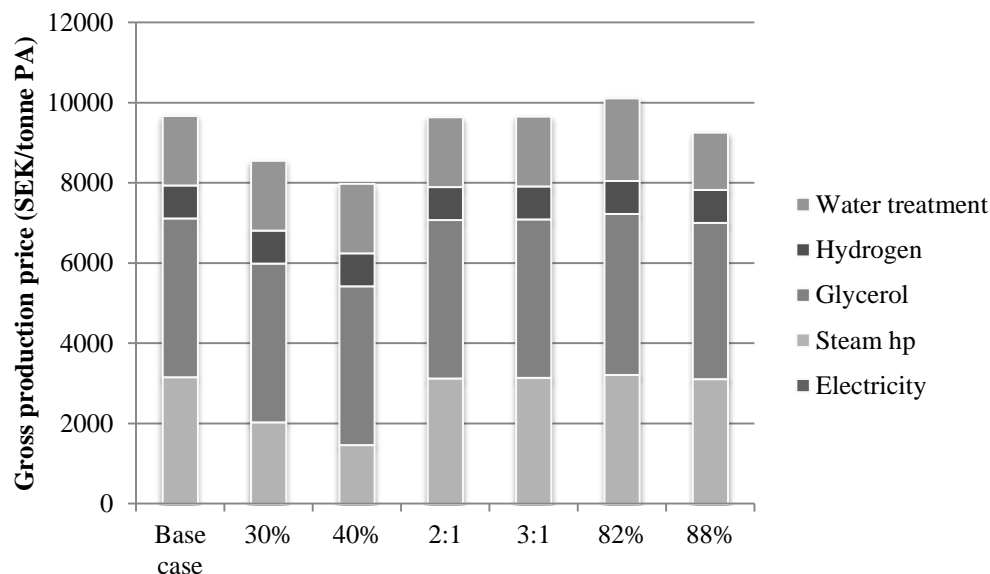


Figure 6.4. Results from gross production price calculations

Table 6.1 contains the numeric results from the gross production price calculations. Prices are listed in ascending order. Energy income refers to the selling of low-pressure steam and district heating.

Table 6.1. Numeric results from gross production price calculations

Scenario	Gross production price (SEK/tonne PA)	Gross production price, including energy income (SEK/tonne PA)
Glycerol concentration 40 %	7982	7470
Glycerol concentration 30 %	8549	7841
Acrolein yield 88 %	9253	8172
Hydrogen-to-glycerol ratio 2:1	9635	8540
Hydrogen-to-glycerol ratio 3:1	9651	8583
Base case	9674	8573
Acrolein yield 82 %	10 108	9360

### 6.2.2 Investment costs

Using the Hand method and cost updates as described in chapter 5, the investment cost for building a propionaldehyde production plant as the one developed by Biofuel-solutions was calculated.

Investment cost = 64.7 MSEK

### 6.2.3 Operating costs

By combining the simulation results from the base case and utility prices from table 5.1, the difference in profit and utility costs was calculated. Then the annuity factor and the additional operation costs could be calculated as described in chapter 5. All calculations are based on a presumed production of 10 000 tonne propionaldehyde per year.

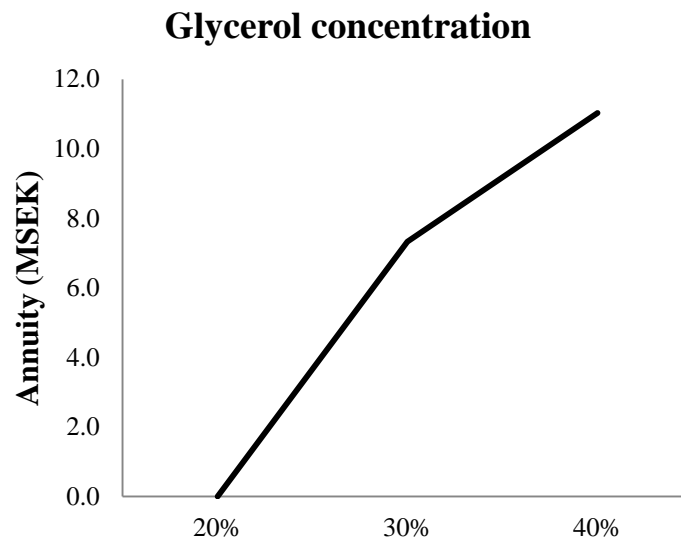
Income – Utility costs = 49.3 MSEK

Annuity factor = 0.13

Additional operating costs = 40.9 MSEK

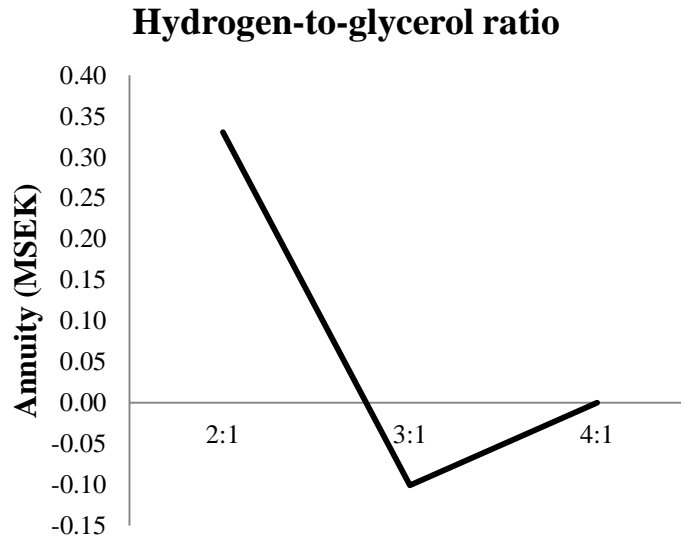
### 6.2.4 Annuity comparison

Figures 6.5-6.7 contains the results from the annuity calculations for each of the different scenarios. In every scenario, there is a case where the annuity equals zero, these cases corresponds to the base case configurations, i.e. the simulation without any modifications.



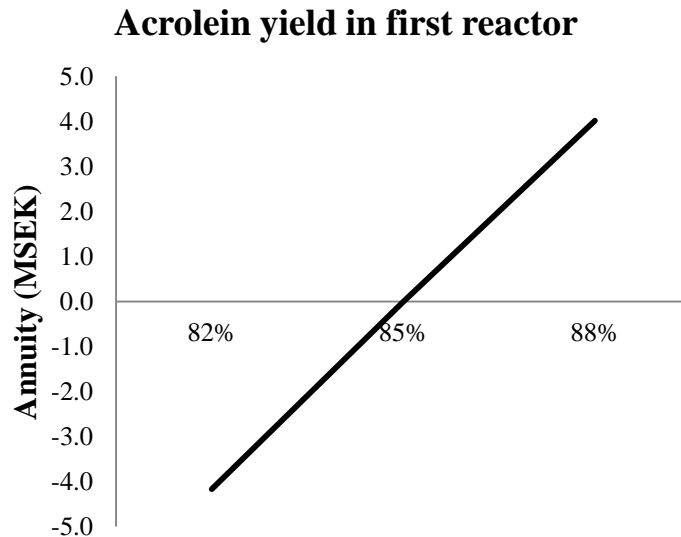
*Figure 6.5. Annuity from scenario with varied glycerol concentration*

The result from the scenario with varied glycerol concentration in the feed, see figure 6.5, clearly shows an increase in profit with an increasing amount of glycerol in the feed. This is due to the drastic decrease in high-pressure steam usage. Even though the income from low-pressure steam and district heating decreases with increasing glycerol concentration, the decrease in high-pressure steam purchase cost is significantly greater. The annuity benefits from a higher glycerol concentration.



*Figure 6.6. Annuity from scenario with varied hydrogen-to-glycerol ratio*

The result from the scenario with varied hydrogen-to-glycerol ratio, see figure 6.6, clearly shows an increase in profit with lower hydrogen-to-glycerol ratios, this corresponds well with the results from the parametric study. As the ratio increases the usage of high-pressure steam and electricity does as well while the production of low-pressure steam decreases. This is believed to be the cause for the reduction in profit. The annuity benefits from a lower hydrogen-to-glycerol ratio.



*Figure 6.7. Annuity from scenario with varied acrolein yield in first reactor*

The result from the scenario with varied acrolein yield in first reactor, see figure 6.7, clearly shows an increase in profit with an increasing with increasing acrolein yield. Even though the income from produced low-pressure steam and district heating decreases throughout the scenario, so does the utility usage and glycerol consumption. The loss of income is surpassed by the decrease in costs. The annuity benefits from a higher acrolein yield.

## 7 Discussion

It has been made clear throughout the different evaluation methods that one parameter in particular has the largest impact on the process profitability, and that is the glycerol concentration in the feed. The parametric study showed that the utility use significantly decreased when the concentration of glycerol in the feed was increased. Even though this also had the effect that the production of profitable utilities decreased, the immense reduction of costly utilities nullified the loss in income as shown in the gross production price and annuity calculations. More trials must be conducted to insure that the catalysts performance still gives satisfactory results when the glycerol concentration is increased.

The process modification that gave the least promising results is the case when the yield of acrolein in the first reactor was decreased from 85 % to 82 %. There were no significantly large changes in utility use when looking at the results from the parametric study, but when turning to the economic evaluations a notable loss in profit could be seen. This process configuration not only holds the highest gross production price but it also causes an economical deficit. A low yield requires a higher amount of reactants to reach the desired production capacity which automatically entails more feed and an increase in utility use.

None of the remaining process modifications leads to any prominent changes in neither utility use or economical deficit or surplus.

To summarize the results it can be said that the best results were obtained when the glycerol concentration in the feed was set to be 40 %. This configuration gave the lowest propionaldehyde gross production price of 7 982 SEK/tonne and an annual annuity surplus of 11.0 MSEK in comparison to the base case. The worst results were obtained when the acrolein yield in the first reactor was set to 82 %. This configuration gave the highest propionaldehyde gross production price of 10 108 SEK/tonne and an annual annuity deficit of 4.0 MSEK in comparison to the base case.

To bear in mind is that numerous assumptions and simplifications that will affect the results have been made throughout the process. These assumptions and simplifications can be found in both the modelling of the process as well as the economic calculations.

Assumptions and simplifications made in the simulation model have the effect that the accuracy of the obtained results must be seriously questioned. By not taking heat loss into consideration, the values regarding the utility use are lower than in reality, which means that the real utility costs are higher than the ones used in the calculations. The same reasoning can be used when considering the absence of a bleed stream and salt in the feed. Other factors that contribute to insecurity are the presumed yields. These have only been tested on a laboratory scale and it is not certain that they are valid on the scale that is used in the simulation model.

The economical calculations do also contain a certain level of insecurity both in the investment and the utility calculations. None of the unit operations have been optimized and the values of used heat transfer coefficient and gas hourly space velocities have not been experimentally determined, only estimated. This means that the size estimations may not be accurate and that wrong equipment has been used when estimating the investment costs. Also, equipment such as pumps and piping has not been included in the model and are therefore missing from the investment cost. Some level of uncertainty can also be found in the Hand method

calculations. The place factor that was used in the calculations is outdated due to the changing economy. Also, the final investment cost was only updated to 2010 year's prices since newer CEPI factors could not be found. Lastly the profit estimations presuppose that the plant is a brown field erection in vicinity of a district heating network. If this is not the case then additional costs must be added for self-production of hydrogen and high-pressure steam and there will be no extra income from produced district heating.

## **7.1 Future work**

This has only been a first glance at a production process that needs to be developed much further and in greater detail before any decision whether to proceed with a pilot plant or to reject the project altogether can be made with certainty.

The next step is further development of the simulation model. This means extending the model to include additional equipment such as pumps and piping and later even more advanced equipment such as automatic control. A more detailed model should also take the heat loss throughout the process and boiling point elevation that occurs in the evaporator into consideration.

Another major aspect when further developing the process is to do a detailed optimization of all unit operations. This entails that kinetics for the reactions have to be researched and that testing is done on a larger scale to ensure that the yields that were obtained on a laboratory scale and used in this simulation are valid on a large scale as well. A pinch analysis should be performed to better optimize the plant's energy use and hopefully reducing the need for certain utilities. The heat exchanger coefficients that were used in the simulation were only estimations based on rules of thumb and should therefore be replaced by more accurate ones provided by e.g. Alfa Laval.

Further simulations should be made with multiple simultaneous process modifications to study possible synergy effects.

If the development advances far enough for it to be considered possible to build a pilot plant it would be appropriate to perform further economic evaluations including looking at equipment quotes from different suppliers. Also, a sensitivity-analysis of the raw material prices should be made.

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# Appendix A

Table A.1-A.3 contains the results from the parametric study. All values are expressed per tonne of produced PA.

*Table A.0.1. Results from simulation with varied glycerol concentration*

<b>Case</b>	<b>Electricity (kWh)</b>	<b>Steam hp (tonne)</b>	<b>Steam lp (tonne)</b>	<b>Cooling water (tonne)</b>	<b>District heating (MWh)</b>	<b>Organic waste (tonne)</b>	<b>Glycerol (tonne)</b>
<b>20%</b>	2.70	11.69	5.12	50.85	1.84	0.12	1.76
<b>30%</b>	2.70	7.53	2.98	39.45	1.36	0.12	1.76
<b>40%</b>	2.70	5.43	1.90	33.77	1.12	0.12	1.76

*Table A.0.2. Results from simulation with varied hydrogen-to-glycerol ratio*

<b>Case</b>	<b>Electricity (kWh)</b>	<b>Steam hp (tonne)</b>	<b>Steam lp (tonne)</b>	<b>Cooling water (tonne)</b>	<b>District heating (MWh)</b>	<b>Organic waste (tonne)</b>	<b>Glycerol (tonne)</b>
<b>2:1</b>	0.93	11.56	5.23	48.98	1.68	0.12	1.76
<b>3:1</b>	1.82	11.61	5.17	49.90	1.76	0.12	1.76
<b>4:1</b>	2.70	11.69	5.12	50.85	1.84	0.12	1.76

*Table A.0.3. Results from simulation with varied acrolein yield in first reactor*

<b>Case</b>	<b>Electricity (kWh)</b>	<b>Steam hp (tonne)</b>	<b>Steam lp (tonne)</b>	<b>Cooling water (tonne)</b>	<b>District heating (MWh)</b>	<b>Organic waste (tonne)</b>	<b>Glycerol (tonne)</b>
<b>82%</b>	2.76	11.88	5.19	51.59	1.88	0.15	1.79
<b>85%</b>	2.70	11.69	5.12	50.85	1.84	0.12	1.76
<b>88%</b>	2.65	11.51	5.04	50.20	1.81	0.10	1.73

## Appendix B

Table B.1 contains the calculations of the production price of propionaldehyde based on utility costs and profit.

*Table B.0.1. Results from calculations of propionaldehyde production price*

Scenario		Glycerol concentration			Hydrogen-to-glycerol ratio		Acrolein yield	
		Base	30%	40%	2:1	3:1	82%	88%
<b>Cost</b>	Electricity	2.70	2.70	2.70	0.93	1.82	2.76	2.64
	Steam hp	3156.96	2031.95	1465.02	3120.07	3134.95	3207.46	3107.99
	Glycerol	3953.15	3953.15	3953.15	3953.15	3953.15	4016.57	3891.68
	Hydrogen	822.15	822.15	822.15	822.15	822.15	822.15	822.15
	Water treatment	1738.83	1738.82	1738.83	1738.83	1738.83	2058.58	1429.02
		9673.79	8548.77	7981.85	9635.13	9650.90	10107.52	9253.48
<b>Gross production price</b>		<b>9674</b>	<b>8549</b>	<b>7982</b>	<b>9635</b>	<b>9651</b>	<b>10108</b>	<b>9253 SEK/tonne PA</b>
<b>Profit</b>	Steam lp	-690.78	-402.17	-257.07	-705.54	-698.63	-330.75	-680.41
	District heating	-409.70	-306.00	-255.00	-389.30	-368.90	-416.50	-401.20
		-1100.48	-708.17	-512.07	-1094.84	-1067.53	-747.25	-1081.61
<b>Gross production price including energy income</b>		<b>8573</b>	<b>7841</b>	<b>7470</b>	<b>8540</b>	<b>8583</b>	<b>9360</b>	<b>8172 SEK/tonne PA</b>

## Appendix C

Investment cost calculations. Table C.1 lists the different factors used in the cost estimations. Table C.2-C.8 contains the results from the individual equipment cost calculations. Table C.9 contains the catalyst cost calculations.

### Investment costs excluding catalyst costs

*Table C.0.1. Correlation factors for investment calculations*

Correction factors	Short	Value
Material adjustment factor	$F_m$	0.55
Instrumentation factor	$F_i$	1.55
Building factor	$F_b$	1.47
Place factor	$F_p$	1.05
Auxiliary buildings and equipment	-	1.25
Construction and contingencies	-	1.15

*Table C.0.2. Results from storage tank calculations*

Unit	Contents	Volume flow (m <sup>3</sup> /h)	Volume (m <sup>3</sup> )	Cost (\$K)
<b>TANK1</b>	Crude glycerol	2.31	277	95.3
<b>TANK2</b>	Water	8.25	990	180.1
<b>TANK3</b>	Propionaldehyde	1.80	216	84.1
<b>TANK4</b>	Waste	9.64	1157	194.7

*Table C.0.3. Results from heat exchanger calculations*

Unit	U (W/(m <sup>2</sup> K))	Area (m <sup>2</sup> )	Cost (\$K)
<b>HEAT2</b>	50	14	10.9
<b>COOL1</b>	50	35	17.3
<b>COOL2</b>	2000	31	16.2
<b>COOL3</b>	150	470	63.3
<b>COOL4</b>	1500	13	10.5
<b>COOL5</b>	500	133	33.6

*Table C.0.4. Results from reactor calculations*

Unit	Molar flow (kmol/h)	GHSV (h <sup>-1</sup> )	Volume (m <sup>3</sup> )	Cost (\$K)
<b>R1</b>	602	1000	13.5	26.7
<b>R2</b>	646	10000	1.45	6.0

Table C.0.5. Results from flash calculations

Unit	Volume (m3)	Cost (\$K)
<b>FLASH</b>	0.375	2.4

Table C.0.6. Results from compressor calculations

Unit	Power (kW)	Cost (\$K)
<b>COMP</b>	3.3	6.8

Table C.0.7. Results from distillation column calculations

Unit	Diameter (m)	Cost (\$K)
<b>DISTL</b>	0.6	10.4
<b>Bubble trays</b>	0.6	2.8

Table C.0.8. Results from evaporator calculations

Unit	U (W/(m <sup>2</sup> K))	Area (m <sup>2</sup> )	Type	Cost (\$K)
<b>HEAT1</b>	1000	37	Falling-film evaporator	728

Estimated costs based 2005 year's prices:

$$\text{Capital cost} = \Sigma[\text{Equipment purchase cost} \cdot (\text{Hand factor} \cdot F_m)] \cdot F_i \cdot F_b \cdot F_p \quad (1)$$

$$\text{Capital cost} = 4\,141\,711 \text{ US\$}$$

$$\text{Investment cost} = \text{Capital cost} \cdot 1.25 \cdot 1.15 \quad (2)$$

$$\text{Investment cost} = 5\,953\,709 \text{ US\$}$$

Conversion to 2010 year's prices:

$$\frac{\text{Cost at time 2}}{\text{Cost at time 1}} = \frac{\text{CEPI at time 2}}{\text{CEPI at time 1}} \quad (3)$$

$$\text{Investment cost} = 7\,128\,920 \text{ US\$}$$

Conversion to Swedish SEK:

$$\text{Exchange rate} = 7 \text{ SEK/US\$}$$

$$\text{Investment cost} = 49\,902\,438 \text{ SEK}$$

## Catalyst investment costs

Table C.0.9. Results from catalysts calculations

Unit	Volume (m <sup>3</sup> )	Price (SEK/m <sup>3</sup> )	Cost (SEK)
Catalyst R1	13.49735	270 000	3 644 285
Catalyst R2	1.448788	450 000	651 954

Estimated catalysts costs:

$$\text{Capital catalyst cost} = \Sigma \text{Catalyst cost} \cdot F_i \cdot F_b \cdot F_p$$

$$\text{Capital catalyst cost} = 10\,278\,431 \text{ SEK}$$

$$\text{Catalyst investment cost} = \text{Capital catalyst cost} \cdot 1.25 \cdot 1.15$$

$$\text{Catalyst investment cost} = 14\,775\,245 \text{ SEK}$$

## Summarized investment costs

$$\text{Total investment cost} = \text{Investment cost} + \text{Catalyst investment cost}$$

$$\text{Total investment cost} = 64\,677\,683 \text{ SEK}$$

## Appendix D

Table D.1 contains the utility and profit calculations for the base case. This is followed by calculation of the annuity factor and the additional operating costs. Table D.2-D.4 contains the annuity calculations for the different simulation scenarios based on utility costs from table 5.1 and tabulated simulation results from table A.1-A.3.

*Table D.0.1. Difference between profit and utility costs for the base case*

<b>Cost</b>	Electricity	-27014
	Steam hp	-31569627
	Glycerol	-39531477
	Hydrogen	-8221500
	Water treatment	-17388266
		<hr/>
		-96737884
<b>Profit</b>	Steam lp	6907839
	District heating	4097000
	Propionaldehyde	135000000
		<hr/>
		146004839
<b>Sum</b>		49266955 SEK
		<b>49.3 MSEK</b>

Annuity factor for an economic lifespan of ten years and a depreciation of 5 %:

$$f_A = \frac{x}{1-(1+x)^{-N}} \quad (5)$$

$$f_A = 0.13$$

Depreciation factor:

$$\text{Depreciation factor} = f_A \cdot G$$

$$\text{Depreciation factor} = 8\,376\,056 \text{ SEK}$$

Additional operating costs providing that the annuity equals zero:

$$\text{Additional operating costs} = \text{Income} - \text{Utility costs} - f_A \cdot G \quad (7)$$

$$\text{Additional operating costs} = 40\,890\,899 \text{ SEK}$$

Table D.0.2. Annuity calculations from simulation with varied glycerol concentration

<b>Case</b>		20%	30%	40%
<b>Cost</b>	Electricity	-27014	-27019	-27017
	Steam hp	-31569627	-20319454	-14650205
	Glycerol	-39531477	-39531499	-39531481
	Hydrogen	-8221500	-8221500	-8221500
	Water treatment	-17388266	-17388243	-17388266
	Additional	-40890899	-40890899	-40890899
	Depreciation factor	-8376056	-8376056	-8376056
		-146004839	-134754670	-129085424
<b>Profit</b>	Steam lp	6907839	4021676	2570744
	District heating	4097000	3060000	2550000
	Propionaldehyde	135000000	135000000	135000000
		146004839	142081676	140120744
<b>Sum</b>		0	7327006	11035320 SEK
		<b>0.0</b>	<b>7.3</b>	<b>11.0 MSEK</b>

Table D.0.3. Annuity calculations from simulation with varied hydrogen-to-glycerol ratio

<b>Case</b>		2:1	3:1	4:1
<b>Cost</b>	Electricity	-9301	-18158	-27014
	Steam hp	-31200671	-31349508	-31569627
	Glycerol	-39531475	-39531536	-39531477
	Hydrogen	-8221500	-8221500	-8221500
	Water treatment	-17388319	-17388322	-17388266
	Additional	-40890899	-40890899	-40890899
	Depreciation factor	-8376056	-8376056	-8376056
		-145618221	-145775979	-146004839
<b>Profit</b>	Steam lp	7055439	6986278	6907839
	District heating	3893000	3689000	4097000
	Propionaldehyde	135000000	135000000	135000000
		145948439	145675278	146004839
<b>Sum</b>		330218	-100701	0 SEK
		<b>0.3</b>	<b>-0.1</b>	<b>0.0 MSEK</b>

Table D.0.4. Annuity calculations from simulation with varied acrolein yield in first reactor

<b>Case</b>		82%	85%	88%
<b>Cost</b>	Electricity	-27563	-27014	-26408
	Steam hp	-32074622	-31569627	-31079908
	Glycerol	-40165688	-39531477	-38916805
	Hydrogen	-8221500	-8221500	-8221500
	Water treatment	-20585807	-17388266	-14290178
	Additional	-40890899	-40890899	-40890899
	Depreciation factor	-8376056	-8376056	-8376056
		-150342135	-146004839	-141801754
<b>Profit</b>	Steam lp	7010513	6907839	6804092
	District heating	4165000	4097000	4012000
	Propionaldehyde	135000000	135000000	135000000
		146175513	146004839	145816092
<b>Sum</b>		-4166622	0	4014338 SEK
		<b>-4.2</b>	<b>0.0</b>	<b>4.0 MSEK</b>